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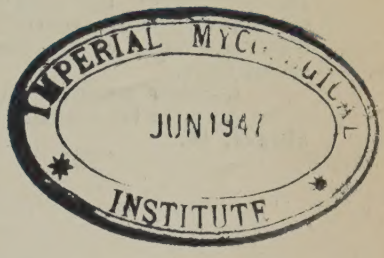


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*10 Août*

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*S. I. VAVILOV*

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# S. I. VAVILOV, President of the Academy

On July 17 a general meeting of the Academy elected a new President to succeed W. L. Komarov, who after many years of fruitful work had resigned his post on account of a severe illness.

His successor, Serghei Ivanovich Vavilov, is one of the most distinguished physicists of this country, the founder of the Soviet school in the domain of luminescence. His literary contribution to the discussion of problems of physical optics comprises about 75 original papers. Taken together, they represent an achievement of fundamental importance. After twenty years of work during which the quenching of luminescence in solutions by different admixtures had been studied, and a theory developed, explaining these phenomena in terms of resonance interaction between molecules, it was found that there are two distinct processes of light emission by organic molecules—a long and a short one. Several laws underlying the phenomenon of polarized luminescence were also brought to light, and it was proved, contrary to the established opinion, that the absolute yield of luminescence in dye-stuff solutions may be very considerable.

Vavilov used the concept of quantum mechanical resonance to build up a theory which gives an adequate quantitative description of many observed fluorescence phenomena, and provides a means of deriving from experimental data the values of the constants characterizing the properties and the behaviour of molecules.

Vavilov has independently suggested a cold source of light which consists in a bulb coated with luminophores and is based on the conversion of ultra-violet radiation, generated by a gas discharge in mercury vapour, into visible light. Under his guidance the technological process of manufacturing gas discharge lamps coated with luminescent compounds has been worked out to a point where it can be introduced into practice.

Another suggestion made and materialized by Vavilov was to study quantum fluctuations of light energy by direct visual observation, making use of the high sensitivity of the eye. In this way he furnished experimental confirmation of the fact that light emission is of quantum discrete character, and established new laws in physiological optics. He is also responsible for outstanding contributions in other domains of optics, above all for the discovery and investigation (carried out in collaboration with Cherenkov, his pupil) of a new fundamental phenomenon—a special kind of light emission, which appears in liquids when electrons are moving in them with a speed exceeding the velocity of light in these liquids.

But the interests of Vavilov as a scholar are not confined to research in the laboratory. He has also a profound knowledge of philosophy and history of science. To the history of Russian science and of this Academy he has always paid particular attention. Among non-specialized readers Vavilov is widely known as the author of many popular writings. These comprise about thirty articles in different magazines and symposiums, and several books. Many more have been written and put into print under his editorship. He has a great love for books. Different publishing enterprises claim his participation in their work as editor or head of physics department. Among them are the Great Soviet Encyclopaedia, a number of physical monthlies, and the popular science series of the Academy.

Vavilov's research work is linked up with his practical endeavour to make optical instruments serve the needs of industry and defence. As director of the Physical Institute of the Academy and scientific director of the State Optical Institute, he paid his closest attention to defence problems which came to the forefront of interest during the years of war. In these years Vavilov showed himself an ardent patriot and developed an intense activity in coping with urgent war problems. In 1943 he was appointed Commissioner of the State Committee of Defence.

Well-known is his rôle in the organization of educational work, his constant attention to new enrollment and creation of adequate training conditions for recruits in the research institutions under his supervision and in the Moscow University. In the domain of optical physics, a large school has already been formed by his associates and pupils.

S. I. Vavilov has made a wide reputation not merely as a progressive scientist, but also as a public man. During the 15 years of his work with the Academy he has been repeatedly elected to various important offices. For many years he was a member of the Leningrad Soviet, and at present he is a deputy of the Supreme Soviet of the RSFSR from the constituency of Vasilievsky Ostrov, Leningrad.

For his services and achievements Vavilov has more than once been honoured by the Government. In 1939 he was awarded the Red Banner of Labour for work in defence industry; in 1943 the Order of Lenin for his activity at the State Optical Institute. In the same year his scientific contributions won him a Stalin prize, and in 1945 the Order of Lenin was conferred upon him for a second time.

«Comptes Rendus» is glad to welcome the promotion of the oldest member of its Editoral Board to the high post of President of the Academy of Sciences of the USSR.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
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*MATHEMATICS*

# GEOMETRY OF FIELD OF LOCAL CURVES IN $X_3$ AND THE SIMPLEST CASE OF LAGRANGE'S PROBLEM IN THE CALCULUS OF VARIATIONS

By V. WAGNER

*(Communicated by A. N. Kolmogoroff, Member of the Academy, 31. V. 1945)*

Consider the simplest case of the problem of Lagrange in the calculus of variations, which consists in finding the extremum of the integral

$$s = \int_{u_1}^{u_2} F(\xi^\alpha, \dot{\xi}^\alpha)\, du, \quad \alpha, \beta, \ldots, \omega = 1, 2, 3 \tag{1}$$

under the condition

$$f(\xi^\alpha, \dot{\xi}^\alpha) = 0 \tag{2}$$

where $F(\xi^\alpha, \dot{\xi}^\alpha)$, $f(\xi^\alpha, \dot{\xi}^\alpha)$ are positive homogeneous functions of the first degree with respect to the variables $\dot{\xi}^\alpha$, and all values of $F(\xi^\alpha, \dot{\xi}^\alpha)$ are positive.

Let us interpret $\xi^\alpha$ as point coordinates in the three-dimensional space $X_3$, and denote by $x^\alpha$ the coordinates of a point in the tangent three-dimensional centro-affine Euclidean space $E_3$ associated with each point of $X_3$.

The equation

$$F(\xi^\alpha, x^\alpha) = 1 \tag{3}$$

determines a surface in each tangent $E_3$, which is the indicatrix of Finslerian metric defined in $X_3$ by the integral (1).

The equation

$$f(\xi^\alpha, x^\alpha) = 0 \tag{4}$$

determines in each tangent $E_3$ a surface which is a locus of rays issuing from the centre of $E_3$. We complete this surface to a conical surface replacing each ray by the whole straight line.

A vector at a point of $X_3$ is said to be admissible if its direction coincides with the direction of a certain rectilinear generator of the corresponding conical surface. The admissible curves of the problem of Lagrange are those whose tangent vectors are admissible. It is obvious that the Finslerian length of arc of admissible curves depends only on the curves in the tangent $E_3$'s determined by the equation (3) and (4) together, but not on the whole Finslerian metric in $X_3$. We call the curves determined by the equations (3) and (4) indicatrices of the problem of Lagrange. It is natural to consider two problems of Lagrange with the coinciding indicatrices as being identical

although given in the ordinary way they may differ one from another by the form of the integrand $F(\xi^\alpha, \dot{\xi}^\alpha)$. In this meaning every problem of Lagrange of the considered kind is determined by giving a field of local curves in $X_3$, *i. e.* by giving a certain curve in each tangent $E_3$.

Let there be given a field of local curves by its parametric equations

$$x^\alpha = l^\alpha(\xi^\lambda, \eta) \tag{5}$$

where the allowable transformations of the parameter are

$$^*\eta = \varphi(\xi^\alpha, \eta) \tag{6}$$

Considering the local curves as one-dimensional local spaces $X_1$'s associated with the points of $X_3$, we obtain a compound manifold $X_{3+(1)}$ [1].

Supposing that the curves of the field are no central plane curves, *i. e.* their planes do not pass through the centre of $E_3$, we shall have the radius-vector of the curve satisfying the differential equation

$$\frac{\partial^3 l^\alpha}{\partial\eta^3} - 3\gamma\frac{\partial^2 l^\alpha}{\partial\eta^2} + \left(3\frac{\partial\gamma}{\partial\eta} - 4p\right)\frac{\partial l^\alpha}{\partial\eta} + \overset{(3)}{w} l^\alpha = 0 \tag{7}$$

where $\overset{(3)}{w}$, $\gamma$, $p$ are one-component geometric objects invariantly connected with the curve. Under the transformations (6) their components transform thus

$$^*\overset{(3)}{w} = \frac{\overset{(3)}{w}}{\varphi'^3}; \quad ^*\gamma = \frac{\gamma}{\varphi'} - \frac{\varphi''}{\varphi'^2}; \quad ^*p = \frac{p}{\varphi'^2} - \frac{\varphi'''}{\varphi'^3} + \frac{3}{2}\frac{\varphi''^2}{\varphi'^4} \tag{8}$$

where the accents denote differentiation with respect to $\eta$.

It follows that $\overset{(3)}{w}$ is a tensor of the third valence, and $\gamma$ is a geometric object of affine connexion in $X_1$. Denoting by $\nabla$ the operator of covariant derivative with respect to $\gamma$, we rewrite (7) thus:

$$\nabla^3 l^\alpha + \overset{(2)}{v}\nabla l^\alpha + \overset{(3)}{w} l^\alpha = 0 \tag{9}$$

where $\overset{(2)}{v} = 4\left(\frac{\partial\gamma}{\partial\eta} - \frac{1}{2}\gamma^2 - p\right)$ is a tensor of the second valence. The covariant vectors $\overset{(-1)}{l}_\alpha$, $\overset{(-2)}{m}_\alpha$, $\overset{(-2)}{n}_\alpha$, which are reciprocal with the contravariant vectors $l^\alpha$, $\nabla l^\alpha$, $\nabla^2 l^\alpha$, are components of tensors in $X_1$ of the valences 0, $-1$, $-2$, respectively. By means of these covariant vectors we define the three Pfaffians $\overset{(-1)}{l} = \overset{(-1)}{l}_\alpha d\xi^\alpha$; $\overset{(-1)}{m} = \overset{(-1)}{m}_\alpha d\xi^\alpha$; $\overset{(-2)}{n} = \overset{(-2)}{n}_\alpha d\xi^\alpha$ and the three bilinear differential forms $\overset{(-3)}{L} = [\overset{(-2)}{m}\ \overset{(-1)}{n}]$, $\overset{(-2)}{M} = [\overset{(-1)}{n}\ \overset{(-1)}{l}]$, $\overset{(-2)}{N} = [\overset{(-1)}{l}\ \overset{(-1)}{m}]$, where the brackets denote the Cartan exterior multiplication of differential forms.

By means of the equation

$$\delta\eta = d\eta + \Gamma = 0 \tag{10}$$

where $\Gamma = \Gamma_\alpha(\xi^\lambda, \eta)\, d\xi^\alpha$ is the given Pfaffian, we introduce in $X_{3+(1)}$ a linear connexion which will determine representations of the local curves along any curve in $X_3$. These representations of the local curves in their turn determine a parallel displacement of admissible vectors in $X_3$.

The bilinear differential form

$$\overset{(-1)}{R} = [\partial\Gamma] - \left[\Gamma\frac{\partial\Gamma}{\partial\eta}\right] \tag{11}$$

where $\partial = d\xi^\alpha\frac{\partial}{\partial\xi^\alpha}$, is said to be the curvature form of connexion, because its identical vanishing means that the representations of the local curves do not depend on the path. $\overset{(-1)}{R}$ is a tensor of the valence $-1$ in $X_1$.

Putting $\overset{(-1)}{R} = \overset{(-2)}{R_L}\overset{(-3)}{L} + \overset{(1)}{R_M}\overset{(-2)}{M} + \overset{(-1)}{R_N}\overset{(-1)}{N}$, we obtain the three ordinary tensors $\overset{(2)}{R_L}$, $\overset{(1)}{R_M}$, $R_N$ in $X_1$ of the valences 2, 1, 0, respectively. By means of the connexion (10) we define the absolute differentiation of fields of local geometric object in $X_{3+(1)}$.

The absolute differentials of the $r$-th valence tensor $\overset{(r)}{g}$ and of the geometric object $\gamma$ are

$$\left.\begin{aligned} \overset{(r)}{Dg} &= \partial \overset{(r)}{g} - \Gamma \frac{\partial \overset{(r)}{g}}{\partial \eta} - r \frac{\partial \Gamma}{\partial \eta} \overset{(r)}{g} \\ D\gamma &= \partial\gamma - \Gamma \frac{\partial \gamma}{\partial \eta} - \frac{\partial \Gamma}{\partial \eta}\gamma - \frac{\partial^2 \Gamma}{\partial \eta^2} \end{aligned}\right\} \qquad (12)$$

$\overset{(r)}{Dg}$ is a tensor of the $r$-th valence, and $D\gamma$ is a tensor of the first valence in $X_1$. For a tensor $\overset{(r)}{\omega}$ in $X_{3+(1)}$ whose component is a linear or bilinear differential form in $X_3$, we define the exterior absolute differential by means of the equation

$$[\overset{(r)}{D\omega}] = [\overset{(r)}{\partial \omega}] - \left[\Gamma \frac{\partial \overset{(r)}{\omega}}{\partial \eta}\right] - r\left[\frac{\partial \Gamma}{\partial \eta} \overset{(r)}{\omega}\right] \qquad (13)$$

Besides the absolute differential $D$ for tensors, we define the total absolute differential $\delta$

$$\overset{(r)}{\delta g} = \overset{(r)}{dg} - r\left(\frac{\partial \Gamma}{\partial \eta} + \gamma \delta\eta\right) \overset{(r)}{g} = \overset{(r)}{Dg} + \delta\eta \nabla \overset{(r)}{g} \qquad (14)$$

Further we shall use the differential operators $D_l$, $D_m$, $D_n$ defined by the symbolical relation $D = lD_l + \overset{(-1)}{m} D_m + \overset{(-2)}{n} D_n$.

An invariant connexion in $X_{3+(1)}$ can be defined by the following conditions:

$$[\overset{(-2)}{n}\, D\, \overset{(-2)}{n}] = 0, \quad [\overset{(-1)}{m}\, D\, \overset{(-2)}{n}] = 0, \quad [\overset{(-1)}{m}\, D\, \overset{(-1)}{m}] = 0 \qquad (15)$$

which give

$$\Gamma = -\nu_N l - \left(\frac{\partial \nu_N}{\partial \eta} + \gamma \nu_N + \frac{1}{2}\nu_M\right) \overset{(-1)}{m} + (\overset{(-2)}{v}\, \nu_N - \mu_M) \overset{(-2)}{n} \qquad (16)$$

where

$$\nu_N = \frac{[\overset{(-2)}{n}\, \partial\, \overset{(-2)}{n}]}{[l\ m\ n]^{(-1)(-2)}}; \quad \nu_M = \frac{[\overset{(-1)}{m}\, \partial\, \overset{(-2)}{n}]}{[l\ m\ n]^{(-1)(-2)}}; \quad \mu_M = \frac{[\overset{(-1)}{m}\, \partial\, \overset{(-1)}{m}]}{[l\ m\ n]^{(-1)(-2)}}$$

The characteristics of the partial differential equation corresponding to the field of local conical surfaces (4) are determined by the equations:

$$\frac{d\xi^\alpha}{ds} = l^\alpha(\xi^\lambda, \eta); \quad \frac{\delta\eta}{ds} = 0 \qquad (17)$$

which means that, from the point of view of a parallel displacement of admissible vectors, they are geodesics.

Let $\overset{v}{d\xi^\alpha}$ be admissible variations of an admissible curve. They satisfy the single condition

$$\frac{\delta\, \overset{(-2)}{n_v}}{ds} + \overset{(-1)}{m_v} \frac{\delta\eta}{ds} = 0 \qquad (18)$$

where we denote $l_v = l_\alpha \overset{v}{d\xi^\alpha}$, $\overset{(-1)}{m_v} = m_\alpha \overset{v}{d\xi^\alpha}$, $\overset{(-2)}{n_v} = n_\alpha \overset{v}{d\xi^\alpha}$.

Supposing that the admissible curve under consideration has no points where the order of contact with the characteristics is more than 1, we can represent the variation of length of arc of the curve thus:

$$\overset{v}{ds} = \left[ l_v - \frac{D_l\gamma}{\frac{\delta\eta}{ds}} \overset{(-2)}{n_v} \right]_{s_1}^{s_2} + \int_{s_1}^{s_2} \left\{ \frac{\delta}{ds}\left( \frac{D_l\gamma}{\frac{\delta\eta}{ds}} \right) + \nabla D_l\gamma - \overset{(3)}{w} \frac{\delta\eta}{ds} \right\} \overset{(-2)}{n_v}\, ds \tag{19}$$

whence we obtain the differential equations of the extremals without using the Lagrange multiplier

$$\frac{d\xi^\alpha}{ds} = l^\alpha(\xi^\lambda, \eta);\ \frac{\delta}{ds}\left( \frac{D_l\gamma}{\frac{\delta\eta}{ds}} \right) + \nabla D_l\gamma - \overset{(3)}{w} \frac{\delta\eta}{ds} = 0 \tag{20}$$

With each point of extremal there is associated the transversal plane determined in the tangent $E_3$ by the covariant vector $e_\alpha = l_\alpha - \frac{D_l\gamma}{\frac{\delta\eta}{ds}} \overset{(-2)}{n_\alpha}$ which passes through the tangent at the corresponding point of the indicatrix. The geometrical meaning of Weierstrass condition is that the indicatrix must lie on one side of the transversal plane.

Every point transformation $'\xi^\alpha = \varphi^\alpha(\xi^\lambda)$ in $X_3$ determines the centro-affine representation $'x^\alpha = \frac{\partial\varphi^\alpha}{\partial\xi^\beta} = x^\beta$ of the tangent $E_3$'s associated with the corresponding points in $X_3$. Two fields of local curves in $X_3$ are said to be equivalent if there exists in $X_3$ a point transformation which determines representations of the tangent $E_3$'s, mapping the curves of the first field on the curves of the second field. To find conditions for the equivalence of two fields of local curves, we have to obtain the complete set of differential invariants for these fields. It can be shown that the complete set of differential invariants of a field of local curves can be expressed in terms of the tensors $\overset{(3)}{w}$, $\overset{(2)}{v}$, $D_l\gamma$, $R_N$, and the tensors derived from them by means of the differential operators $D_l$, $D_m$, $D_n$, $\nabla$. If the curves of the field are not plane, *i. e.* $\overset{(3)}{w} \neq 0$, the scalar $R_N$ can be also expressed in terms of the tensors $\overset{(3)}{w}$, $\overset{(2)}{v}$, $D_l\gamma$ and their derivatives.

A field of local curves is said to be constant if it is possible to choose a system of coordinates in $X_3$ in such a way that the equations (5) of the local curves do not involve $\xi^\alpha$. It can be shown that a necessary and sufficient condition that a field of local curves be constant is that the connexion (16) be of zero curvature, and the geometric objects $\overset{(3)}{w}$, $\overset{(2)}{v}$, $\gamma$ form the constant fields of local geometric objects in $X_{3+(1)}$.

Using some identities for the connexion (16) we find that this condition can be expressed by the equations

$$D_l\gamma = 0;\quad D\overset{(3)}{w} = 0;\quad D\overset{(2)}{v} = 0;\quad R_N = 0. \tag{21}$$

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REFERENCES

[1] V. Wagner, C. R. Acad. Sci. URSS, XL, No. 3 (1943).

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*MATHEMATICS*

# ON THE DUALITY LAW IN NORMAL SPACES

By G. CHOGOSHVILI

*(Communicated by A. N. Kolmogoroff, Member of the Academy, 19. IV. 1945)*

§ 1. Definitions. A set $M$ of the normal space $R$ is said to be bicompactly situated in $R$, if for every open and bicompact in $M$ (cf. (2)) subset $O_M$ of the set $M$ there exists such an open and bicompact in $R$ set $O$ of the space $R$ that $O_M = O \cap M$. We shall say that the set $M$ possesses a domain of closure, if there exists such an open set $O$ that $M$ is contained and closed in $O$.

A pair of mutually complementary sets $A$ and $B = R - A$ of the space $R$ shall be called an admissible pair of sets, if $A$ is bicompactly situated in $R$ and if the verges (cf. (1), p. 40) $a$ and $b$ of the sets $A$ and $B$ possess domains of closure.

A set $O$, open in $R$, shall be called: 1) inner with respect to $A$, if $\bar{O} \subset A$; 2) a boundary set with respect to $A$, if $O \subset A$, but $\bar{O} \not\subset A$; 3) a verging set with respect to $A$, if $O \cap a$ is non-void and closed in $O$, while $O \cap b$ is either void, or not closed in $O$. A set $O$ shall be called admissible with respect to $A$, if it is either an inner, or a boundary, or a verging set with respect to $A$. $O$ is singular with respect to $A$, if $O \cap A$ is not bicompact in $A$. A finite open covering $O_\alpha$ of the space $R$ is said to be admissible with respect to $A$, if the subsystem $O_\alpha^A$ of the sets $O_\alpha$, admissible with respect to $A$, covers $A$. If $O_\alpha$ is admissible with respect to $A$, then the system of intersections of the sets from $O_\alpha^A$ with $A$ forms a covering of $A$, which shall be called induced by $O_\alpha$ on $A$.

A covering $O_\alpha$ of the space $R$ is called transmitting, if:

(A1) Every set from $O_\alpha$ is admissible either with respect to $A$, or with respect to $B$.

(A2) $O_\alpha$ is admissible with respect to $A$.

(A3) If $O'_\alpha, \ldots, O''_\alpha$ are sets from $O_\alpha$ admissible with respect to $A$, and if $O'_\alpha \cap \ldots \cap O''_\alpha \neq 0$, then also $O'_\alpha \cap \ldots \cap O''_\alpha \cap A \neq 0$.

(A4) $O_\alpha$ does not contain boundary sets with respect to $B$.

(A5) None of the singular sets from $O_\alpha$, admissible with respect to $B$, intersects with any non-singular and admissible with respect to $A$ set from $O^\alpha$.

(A6) Every non-singular and admissible with respect to $A$ set from $O_\alpha$ is bicompact in $R$.

A covering $O_\beta$ of the space $R$ is called receiving, if:

(B1) $O_\beta$ consists of sets admissible either with respect to $A$, or with respect to $B$.

(B2) $O_\beta$ is admissible with respect to $A$, as well as with respect to $B$.

(B3) There exists such a transmitting covering $O_\alpha$, that $O_\beta$ is inserted in $O_\alpha$ in such a way that every set from $O_\beta$, intersecting with some singular and admissible with respect to $B$ set from $O_\beta$ contained in a set from $O_\alpha$ admissible with respect to $B$, is itself contained in a set from $O_\alpha$, either admissible with respect to $B$, or singular and admissible with respect to $A$. In this case $O_\beta$ is said to be a covering receiving from $O_\alpha$.

§ 2. Lemmas. In the sequel we assume that $R$ is a totally normal space, and $A$ and $B$, an admissible pair of sets, or that $R$ is a normal space, and $A$ is a set closed and bicompactly situated in $R$. The admissibility and other properties of the coverings are considered with respect to a fixed pair $A$, $B$. The following lemmas hold.

1. For every covering $O_\alpha$ of the space $R$ and covering $U_\lambda$ of the subspace $A$ there exists such a transmitting covering $O_\beta$ which is inserted in $O_\alpha$ and which induces on $A$ a covering inserted in $U_\lambda$.

2. For every transmitting covering $O_\alpha$ and covering $V_\lambda$ of the subspace $B$ there exists a covering $O_\beta$ receiving from $O_\alpha$, which induces on $B$ a covering inserted in $V_\lambda$.

3. For any two transmitting coverings $O_\alpha$ and $O_\beta$ there exists a transmitting covering $O_\gamma$ inserted in them, such that the subsystem $O_\gamma^A$ of sets of the system $O_\gamma$ admissible with respect to $A$ is inserted in the corresponding subsystems $O_\alpha^A$ and $O_\beta^A$.

4. For any two receiving coverings $O_\alpha$ and $O_\beta$ there exists such a receiving covering $O_\gamma$ inserted in them, that the subsystem $O_\gamma^B$ of sets from $O_\gamma$ admissible with respect to $B$ is inserted in analogous subsystems $O_\alpha^B$ and $O_\beta^B$.

§ 3. Homomorphism $H_\nabla$. Duality law. Let

$$\nabla^r(A, X) = \varinjlim \left\{ \nabla^r(K_\alpha - C_\alpha, X), \underset{A^{\alpha\beta}}{\pi^\alpha_\beta} \right\}$$

be the Alexandroff $r$-dimensional $\nabla$-group of homologies of the subspace $A$ by discrete group of coefficients $X$ (cf. ([2]), p. 40, where this group is called the inner Betti group); $K_\alpha$ denotes the nerve of a certain covering $U_\alpha$ of the space $A$; $C_\alpha$, the subcomplex of $K_\alpha$, consisting of vertices corresponding to singular with respect to $A$ sets of the covering $U_\alpha$; $\underset{A^{\alpha\beta}}{\pi^\alpha}$, the homomorphism, defined in the usual way, of the $\nabla$-group of homologies $\nabla^r(K_\alpha - C_\alpha, X)$ into the group $\nabla^r(K_\beta - C_\beta, X)$; $\nabla^r(A, X)$, the limit group of the direct spectrum of $\{\nabla^r(K_\alpha - C_\alpha, X), \underset{A^{\alpha\beta}}{\pi^\alpha_\beta}\}$.

Take an arbitrary element $h^r_A$ from $\nabla^r(A, X)$ and any cycle $z^r_{A\alpha}$ from $h^r_A$ defined on the nerve $K_\alpha$ of the covering $U_\alpha$. $K_\alpha$ may be considered as a subcomplex of the complex $N_\alpha$, being the nerve of the transmitting covering $O_\alpha$ which induces on $A$ the covering $U_\alpha$. Let $E^{K_\alpha}_{N_\alpha} z^r_{A\alpha}$ be the chain of the complex $N_\alpha$ coinciding with $z^r_{A\alpha}$ on the simplexes of $K_\alpha$ and equal to zero on the remaining simplexes of $N_\alpha$ (cf. ([3]), p. 26). Take any covering $O_\beta$ receiving from $O_\alpha$, and consider on the nerve $N_\beta$ of it the $\nabla$-boundary of the projection $\pi^\alpha_\beta E^{K_\alpha}_{N_\alpha} z^r_{A\alpha}$ of the chain $E^{K_\alpha}_{N_\alpha} z^r_{A\alpha}$. Let $V_\beta$ be the covering of the subspace $B$ induced by the covering $O_\beta$, and $L_\beta$, the nerve of $V_\beta$. Consider $L_\beta$ as a subcomplex of $N_\beta$ and define on it the chain $z^{r+1}_{B\beta} = I^{N_\beta}_{L_\beta} \nabla \pi^\alpha_\beta E^{K_\alpha}_{N_\alpha} z^r_{A\alpha}$, being a chain assuming the values $\nabla \pi^\alpha_\beta E^{K_\alpha}_{N_\alpha} z^r_{A\alpha}$ on the simplexes of $L_\beta$. It may be proved that $z^{r+1}_{B\beta}$ is a cycle of the complex $L_\beta$ lying (cf. ([3]), p. 12) on $L_\beta - D_\beta$, where $D_\beta$ is the subcomplex of $L_\beta$ corresponding to sets of the covering $V_\beta$ singular with respect to $B$. It may be further proved that if $z^r_{A\alpha}$ is homologous to zero on $K_\alpha - C_\alpha$, then $z^{r+1}_{B\beta}$ will be homologous to zero on $L_\beta - D_\beta$.

Take the pencil $h_B^{r+1}$ of the Alexandroff $(r+1)$-dimensional $\nabla$-group of homologies of the space $B$: $\nabla^{r+1}(B, X) = \varinjlim \left\{ \nabla^{r+1}(L_\beta - D_\beta, X), \pi_{B^\gamma}^{\beta} \right\}$ containing the cycle $z_{B\beta}^{r+1}$. Let us correlate this element $h_B^{r+1}$ of the group $\nabla^{r+1}(B, X)$ to the original element $h_A^r$ of the group $\nabla^r(A, X)$. The correspondence $H_\nabla$ thus established by means of the operators $E_{N\alpha}^{K\alpha}$, $\pi_\beta^\alpha$, $\dot{\nabla}$, $I_{L_\beta}^{N_\beta}$ is regular in the sense that it does not depend neither on the choice of $z_{A\alpha}^r$ from $h_A^r$, nor on the choice of the one or the other transmitting or receiving covering, nor on the form of the simplicial representation of the nerve of the latter into the nerve of the former. The representation $H_\nabla$ is a homomorphism of the group $\nabla^r(A, X)$ into the group $\nabla^{r+1}(B, X)$. Let $\nabla_0^r(A, X)$ be the nucleus of this homomorphism, $\nabla_*^r(A, X)$, the factor-group of the group $\nabla^r(A, X)$ by the subgroup $\nabla_0^r(A, X)$; and ${}_*\nabla^{r+1}(B, X)$, the subgroup $H_\nabla \nabla^r(A, X)$ of the group $\nabla^{r+1}(B, X)$ covered by $H_\nabla$. Between the groups $\nabla_*^r(A, X)$ and ${}_*\nabla^{r+1}(B, X)$ exists an isomorphism $S_\nabla$

$$\nabla_*^r(A, X) \approx {}_*\nabla^{r+1}(B, X)$$

In the case where $r$- and $(r+1)$-dimensional Alexandroff $\nabla$-groups of homologies of the normal space $R$ are nul-groups, and where $A$ is a closed in $R$ set, bicompactly situated in $R$, then $\nabla_0^r(A, X)$ is a nul-subgroup of $\nabla^r(A, X)$, and ${}_*\nabla^{r+1}(B, X)$ coincides with $\nabla^{r+1}(B, X)$, so that $H_\nabla$ establishes an isomorphism between the groups $\nabla^r(A, X)$ and $\nabla^{r+1}(B, X)$. If $R$ is a locally bicompact space, this yields the duality law of Alexandroff-Kolmogoroff ([3,4]). The groups $\nabla^r(A, X)$ and $\nabla_0^r(A, X)$ enable us, in general, to find out the situation of $A$ in $R$.

§ 4. Infinite Coverings. Let $O = \{O_\alpha\}$ be the system of all locally finite open coverings of the space $R$. We shall call the coverings $O_\alpha$ and $O_\beta$ from $O$ equivalent, if every set from $O_\alpha$ intersects with not more than a finite number of sets from $O_\beta$, and *vice versa*. This definition decomposes the system $O$ into classes $O^\tau$ of equivalent coverings. The coverings of every class $O^\tau$ induce on $A$ (on $B$) coverings of the subspace $A(B)$ belonging to one and the same class $O_A^\tau$ ($O_B^\tau$) of the system of coverings of $A(B)$, in the sense of the above definition of classes applied to $A$ (to $B$). $O_A^\tau$ and $O_B^\tau$ are in this case called adjoined classes of coverings of the subspaces $A$, respectively $B$.

By Alexandroff $r$-dimensional $\nabla$-group of homologies of the space $R$, corresponding to the class $O^\tau$ of coverings of $R$, we shall call the limit group $\nabla_\tau^r(R, X)$ of the direct spectrum $\{\nabla^r(N_\alpha - E_\alpha, X), \pi_\beta^\alpha\}$, where $N_\alpha$ is the nerve of the covering $O_\alpha$ from $O^\tau$; $E_\alpha$ is the subcomplex of $N_\alpha$ corresponding to sets from $O_\alpha$, singular with respect to $R$; $\nabla^r(N_\alpha - E_\alpha, X)$ is the $r$-dimensional $\nabla$-group of homologies of finite (*i. e.* differing from zero only on a finite number of simplexes) chains lying on $N_\alpha - E_\alpha$; and, finally, $\pi_\beta^\alpha$ is the homomorphism of the group $\nabla^r(N_\alpha - E_\alpha, X)$ into the group $\nabla^r(N_\beta - E_\beta, X)$ defined in the usual way. Let $O_A^\tau$ and $O_B^\tau$ be some adjoined classes of covering of the subspaces $A$ and $B$; and $\nabla_\tau^r(A, X)$ and $\nabla_\tau^r(B, X)$, the corresponding to these classes Alexandroff $\nabla$-groups of homologies of the spaces $A$ and $B$. Then there exists a homomorphism $H_\nabla^\tau$ of the group $\nabla_\tau^r(A, X)$ into the group $\nabla_\tau^{r+1}(B, X)$, analogous to the homomorphism $H_\nabla$ established above in the case of a class of finite coverings.

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REFERENCES

[1] P. Alexandroff u. Hopf, Topologie, 1935. [2] A. Kolmogoroff, C. R., 202 (1936). [3] П. С. Александров, Уч. Зап. МГУ, 45 (1940). [4] P. S. Alexandroff, Bull. Acad. Sci. URSS, sér. math., 6 (1942).

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*MECHANICS*

# DAMPING OF THE ROTATION OF A PROJECTILE IN PIERCING A VISCOUS MEDIUM

By S. M. TARG

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Let all the half-space beneath a plane $z = \text{const}$ be filled with some medium. At the moment $t = 0$ a projectile begins to pierce this medium with a velocity of $U$, its angular velocity around its own axis at the initial moment being $\omega_0$. It is assumed that the axis of the projectile always remains parallel to the axis $Oz$. The generatrix of the projectile is given by the equation $r = f(z)$. It is required to determine the law according to which the projectile's angular velocity varies.

While the projectile is piercing the medium, each point $M$ of its surface will be acted upon by a friction force whose direction will be opposite to the component of the velocity at that point lying in a plane tangential to the surface of the projectile. This component $u$ will be composed of the projection of the velocity $U$ onto a tangent to the generatrix of the projectile and the velocity of rotation $\omega r$, and will equal

$$u = \sqrt{\omega^2 r^2 + \frac{U^2}{1 + r'^2}} \tag{1}$$

Denoting the force of friction per unit surface at a given point $M$ by $\tau$, let us find the moment of the force of friction around the axis of the projectile. Since the force $\tau$ is directed opposite to the velocity $u$, its projection onto a plane, perpendicular to the axis of the projectile, will be equal to

$$-\tau \frac{\omega r}{u}$$

Multiplying this value by $r d\sigma$, where $d\sigma$ is an element of the projectile's surface, and taking the integral over the whole surface of that part of the projectile which is immersed, we get the value of the moment we were seeking

$$M = -\omega \int\int_{\sigma} \frac{\tau r^2 \, d\sigma}{u}$$

Denoting the moment of inertia of the projectile around the axis of rotation by $J$ and applying the angular momentum theorem, we get the differential equation of rotation of the projectile in the following form

$$J \frac{d\omega}{dt} = -\omega \int\int_{\sigma} \frac{\tau r^2 \, d\sigma}{u} \tag{2}$$

In order to solve the problem we have set, it is necessary to establish the law of variation of $\tau$ over the surface of the immersed part of the projectile.

It is quite evident that the damping of the rotation of the projectile cannot be due to coulombic friction, therefore we shall assume that it is due to viscous friction.

From the solution of the problem on the penetration of a disc into a viscous medium ([1]) we know that for such a case

$$\tau = \sqrt{\frac{\mu\rho}{\pi}}\, u^{3/2} l^{-1/2} \tag{3}$$

where $\rho$ is the density; $\mu$, the viscosity coefficient; and $l$, the distance of the given point from the lower edge of the disc.

We shall assume that in our case $\tau$ varies by the same law, that $l$ in our case is the distance of the point $M$ from the vertex of the projectile, measured along the trajectory of the particle which at the given moment is located at point $M$, and that $u$ is the velocity determined from equation (1).

In order to determine the value of $l$ it should be noted that between $dl$ and an element of the generatrix of the projectile

$$ds = \sqrt{1+r'^2}\, dz \tag{4}$$

there exists a relation, *viz.*:

$$dl = \frac{u\sqrt{1+r'^2}}{U}\, ds$$

Hence, substituting for $u$ and $ds$ their values from (1) and (4), and integrating with respect to $z$, we find that

$$l = \int_0^z \sqrt{\frac{\omega^2 r^2}{U^2}(1+r'^2) + r'^2 + 1}\, dz \tag{5}$$

Now, substitute for $\tau$ in equation (2) its value from (3). If the depth of penetration at the given moment is $h$, then $\frac{d\omega}{dt}$ can be substituted by $U\frac{d\omega}{dh}$.

Substitute for $u$ and $ds$ their values from (1) and (4) and replace $d\sigma$ by $r\,d\varphi\,ds$. Integrating with respect to $\varphi$, we get the following equation

$$J\frac{d\omega}{dh} = -2\sqrt{\frac{\pi\rho\mu}{U}}\,\omega \int_0^h \frac{r^3}{\sqrt{l}} \sqrt[4]{\frac{\omega^2 r^2}{U^2}(1+r'^2) + r'^2 + 1}\, dz \tag{6}$$

where $l(z)$ can be determined from expression (5), and $r(z)$ is given.

Integrating equation (6) we get the law of damping of rotation in the form $\omega = \omega(h)$. If the law of variation of $U$ in time is known, we can find $\omega = \omega(t)$ on the basis of this solution.

Since practically $U$ is always much greater than $\omega r$, the following approximate equation can be deduced for this case

$$J\frac{d\omega}{dh} = -2\sqrt{\frac{\pi\rho\mu}{U}}\,\omega \int_0^h \frac{r^3}{\sqrt{l}} \sqrt[4]{1+r'^2}\, dz \tag{7}$$

where

$$l = \int_0^z \sqrt{1 + r'^2}\, dz$$

To illustrate this let us consider two particular cases.

1. The sinking body is a cylinder. Assuming that $r = R$, we find from (5) and (6) the following law for the damping of the angular velocity:

$$\omega = \omega_0 \exp\left(-\frac{8}{3}\sqrt{\frac{\pi\mu\rho}{U}}\frac{R^3}{J}h^{3/2}\right) \tag{8}$$

2. The sinking body is a cylinder with radius $R$ and with a conical headpiece. Denoting the height of the conical part by $a$ and the angle at the vertex by $2\alpha$, and considering that in this case $U \gg \omega r$, we find from (7)

$$\left.\begin{aligned} \omega &= \omega_0 \exp\left(-\frac{8}{63}\sqrt{\frac{\pi\mu\rho}{U}}\frac{\operatorname{tg}^3\alpha}{J}h^{4.5}\right) \quad \text{when } h \leqslant a \\ \omega &= \omega_0 \exp\left\{-\frac{4}{J}\sqrt{\frac{\pi\mu\rho}{U}}\left[\frac{2}{63}a^{4.5}\operatorname{tg}^3 + \frac{1}{7}a^{3.5}\operatorname{tg}^3\alpha + \right.\right. \\ &\quad \left.\left. + \frac{2}{3}R^3\sqrt{h-a}\,(h-a)\right]\right\} \quad \text{when } h > a \end{aligned}\right\} \tag{9}$$

Notwithstanding the approximate nature of these assumptions, the results we have come to still make it possible to estimate the damping of the rotation of a projectile as a function of its geometrical parameters and of several of the properties of the medium. In particular, from these results it follows that a change in the rate of penetration of the projectile $U$ should have but little effect upon the damping of its rotation as the depth increases (especially for high values of $\mu$), since in formulae (8) and (9) $U$ is in a power of 0.5, while the power of $h$ is 1.5 and 4.5. The same results show that increase of the calibre of the projectile slows down the damping of rotation, seeing that $J$ increases in proportion to the fifth power of the calibre.

In order to get more authentical quantitative results from these equations, we must have at our disposal more accurate data regarding the values of the viscosity coefficient $\mu$. These data may be obtained by means of the experiments mentioned in the paper cited above [1].

As an example, let us compute the damping of the rotation of a 37-mm projectile when penetrating a metal plate, assuming the value $\mu \approx 13 \cdot 10^8$ poise, given in the International Critical Tables, to be correct.

Considering the headpiece as a cone, we have for it: $a = 35$ mm, and $\operatorname{tg}\alpha = 0.529$. Assuming $U = 650$ m/sec., we find from formula (9) that, after penetrating the plate to a distance of $h = a = 33$ mm, the projectile's angular velocity will be $\omega = 0.05\,\omega_0$, *i. e.* it will practically stop rotating.

If we assume that upon penetrating the plate the projectile's velocity drops to zero, and if we substitute for $U$ its mean value $U_{\text{mean}} = 325$ m/sec., we find that in this case $\omega \doteq 0.05\omega_0$ when $h = 35$ mm. This goes to confirm the conclusion drawn above that change in the velocity $U$ has little effect upon the damping of the projectile's velocity with the depth.

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REFERENCES

[1] N. A. Slezkin, C. R. Acad. Sci. URSS, XLVI, No. 1 (1945).

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*HYDRODYNAMICS*

# CONDITIONS AT THE FRONT OF A TRANSLATION WAVE DISTURBING A STEADY MOTION OF A REAL FLUID

By V. V. WEDERNIKOW

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Let us consider the motion of a continuous wave. The equations of a gradually varying unsteady motion of a real fluid in open channels are of the following form ([1]):

the continuity equation is

$$\frac{\partial Q}{\partial s}+\frac{\partial F}{\partial t}=0 \tag{1}$$

and the dynamics equation is

$$-\frac{1}{B}\frac{\partial F}{\partial s}=\frac{U^2}{C^2R}-i_0+\frac{\alpha}{g}U\frac{\partial U}{\partial s}+\frac{\alpha}{g}\frac{\partial U}{\partial t} \tag{2}$$

Making use of the continuity equation, we can rewrite the dynamic equation as follows ([2]):

$$\frac{\partial F}{\partial s}\left(U^2-\frac{\partial F}{\alpha B}\right)=\frac{\partial Q}{\partial t}-2U\frac{\partial F}{\partial t}+\frac{gF}{\alpha}\left(\frac{U^2}{C^2R}-i_0\right) \tag{3}$$

In the sequel a formula of the Manning type $C^2=R^3/n^2$ will be used for the coefficient $C$ * and we shall adopt the notations $1-\frac{1}{3}\frac{F}{B}\frac{dB}{dF}=N$ and $1-R\frac{d\chi}{dF}=1-2\frac{R}{b}\sqrt{1+m^2}=M$, supposing, in order to simplify the calculation, that the channels have a prismatic form.

By introducing a function whose meaning is determined by the continuity equation, the equation (3) can be reduced to a partial differential equation of the second order, which is not linear in the general case. The trajectory of the front of translation wave disturbing a steady flow is a characteristic ([3]). Along the characteristic the partial derivative cannot in general be computed. It is known, however, that if the condition establishing a relation between the independent variables and the first derivatives, with respect to these variables, of the function sought-for (in the present case, between $s$, $t$, $dt/ds$, $F$, $Q$, $dF/ds$, $dQ/ds$) is fulfilled, then one of the partial derivatives remains arbitrary, and it is possible to compute the derivatives along the characteristic.

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* The results will not be affected essentially, if another type of formula instead of the Manning type is used, or, in general, if the term $U^2/C^2R$ is replaced by a different form of resistance law, bringing on different relations (for instance, that of Bazin) or a different power of $U$ in the equations (2) and (3).

Let us show that this condition is fulfilled at the front of a wave disturbing a steady flow. A convenient way of computing the derivatives will also be indicated, and the formulae will be derived for computing the derivatives of the first and second order in equation (3) for any distance of the front from the initial section.

In the initial section ($s=0$) either the hydrograph $Q=Q_i(t)$ or the water-gauge graph $H=H_i(t)$ is known, *i. e.* $F=F_i(t)$.

The fundamental condition at the wave-front, from which follow all the other conditions and which takes place in virtue of the fact that the initial motion is a steady one (the discharge is a constant all along the flow), is as follows:

$$Q=Q_i=\text{const};\ dQ/dt=0;\ d^2Q/dt^2=0,\ etc. \tag{4}$$

The relation between $s$ and $t$ is established through the introduction of the propagation velocity $W$ of a point of the wave-front along the free surface of the steady flow. Then

$$s=\int_0^t W dt \tag{5}$$

and from (4) and (1) we have

$$\frac{\partial Q}{\partial t}=-W\frac{\partial Q}{\partial s}=W\frac{\partial F}{\partial t} \tag{6}$$

$$\frac{\partial^2 Q}{\partial t^2}=2W\frac{\partial^2 F}{\partial t^2}+W^2\frac{\partial^2 F}{\partial t\,\partial s}+\frac{dW}{dt}\frac{\partial F}{\partial s} \tag{7}$$

*etc.* The velocity of propagation of the wave-front coincides with the velocity $\omega_Q$ of constant discharge.

Let us find the relation between $dF/dt$ and $s$, and from it establish the relation between $F$, $U=Q/F$, $s$, $t$ and $ds/dt=W$. The velocity of the propagation of the wave-front is defined by a well-known formula ([3])

$$W=U\pm\sqrt{\frac{gF}{\alpha B}} \tag{8}$$

In the case of a uniform motion ($dF/dt=0$) the velocity of the front $W$ coincides also with the velocity $\omega$ of propagation of constant area $F$ (or constant depth $H$).

For a steady gradually varying non-uniform flow in prismatic channels the relation between $s$ and $F$, or between $s$ and $U$ is defined by the equation of Belanger ([4])

$$\frac{dF}{ds}=\frac{gF}{\alpha}\left(\frac{U^2}{C^2R}-i_0\right)\Big/\left(U^3-\frac{gF}{\alpha B}\right) \tag{9}$$

The velocity $W$ can therefore be computed for any position of the front. Accordingly, the relations between $s$, $t$ and $ds/dt$ and also between $F$ and $t$ are known, too (the latter relation for $\beta=0$ can be computed from the tables given in ([3])).

For the general case of non-uniform motion we have:

$$\frac{dF}{dt}=\frac{\partial F}{\partial s}W+\frac{\partial F}{\partial t} \tag{10}$$

Hence

$$\frac{\partial F}{\partial t}=W\left(\frac{dF}{ds}-\frac{\partial F}{\partial s}\right);\quad \frac{\partial Q}{\partial t}=W^2\left(\frac{dF}{ds}-\frac{\partial F}{\partial s}\right) \tag{11}$$

For the derivative which remains arbitrary we, respectively, choose $\partial F/\partial s=r$, $\partial^2 F/\partial s^2=\delta$, *etc.* These derivatives characterize the shape of the free surface (its inclination to the bed, its curvature, *etc.*). Construct the differential equation for the derivative $\partial F/\partial s=r$. We shall have

$$\frac{dr}{dt}=\frac{\partial^2 F}{\partial s^2}W+\frac{\partial^2 F}{\partial s\,\partial t} \tag{12}$$

$$\frac{\partial^2 F}{\partial t^2}=\frac{d^2F}{dt^2}-2W\frac{dr}{dt}-\frac{dW}{dt}\frac{\partial F}{\partial s}+W^2\frac{\partial^2 F}{\partial s^2} \tag{13}$$

$$\frac{\partial^2 Q}{\partial t^2}=2W\frac{d^2F}{dt^2}-3W^2\frac{dr}{dt}-3W\frac{dW}{dt}r+\frac{dW}{dt}\frac{dF}{dt}+W^3\frac{\partial^2 F}{\partial s^3} \tag{14}$$

Let us differentiate both sides of equation (3) with respect to $s$. Making use of the continuity equation (1) we get:

$$\begin{aligned}\frac{\partial^2 F}{\partial s^2}\left(U^2-\frac{gF}{\alpha B}\right)=&-\frac{\partial^2 F}{\partial t^2}+\frac{2}{F}\left(\frac{\partial F}{\partial t}\right)^2+\frac{\partial F}{\partial s}\left\{\frac{6U}{F}\frac{\partial F}{\partial t}+\right.\\&\left.+\left(\frac{3U^2}{F}-\frac{gF}{\alpha B^2}\frac{dB}{\partial F}\right)\frac{\partial F}{\partial s}-\frac{1}{F}\frac{\partial Q}{\partial t}-\frac{g}{\alpha}\frac{U^2}{C^2R}[2+M(1+\beta)]\right\}-\\&-\frac{g}{\alpha}\frac{2U}{C^2R}\frac{\partial F}{\partial t}-2U\frac{\partial^2 F}{\partial s\,\partial t}\end{aligned} \tag{15}$$

By means of (8), (9), (11) and (12) we obtain for $r$ an ordinary differential equation of the first order in the general form

$$\begin{aligned}\frac{dr}{dt}=&\frac{3}{4}\frac{W^2}{2U-W}\frac{N}{F}\left(\frac{dF}{ds}\right)^2+\frac{W}{4F}\left(9+\frac{F}{B}\frac{dB}{dF}\right)\frac{dF}{ds}r-Er-\\&-\frac{3}{2}\frac{W-U}{F}Nr^2-\frac{g}{\alpha}\frac{UW}{C^2R(2U-W)}\left[1+\frac{M(1+\beta)U}{2(W-U)}\right]\frac{dF}{ds}\end{aligned} \tag{16}$$

Here and henceforth

$$E=\frac{g}{\alpha}\frac{U}{C^2R}\left[1-\frac{M(1+\beta)U}{2(W-U)}\right] \tag{17}$$

From equation (16) $r$ can be computed for any position of the front, since the value of $r_i$ at point $(s=0,\ t=0)$ is determined, according to the condition (11), by the formula

$$r_i=\left(\frac{\partial F}{\partial s}\right)_i=\left(\frac{dF}{ds}\right)_i-\frac{1}{W_i^2}\left(\frac{\partial Q}{\partial t}\right)_i \tag{18}$$

We proceed to construct the differential equation for the derivatives $\partial^2 F/\partial s^2=\delta$. We shall have

$$\frac{d\delta}{dt}=\frac{\partial^3 F}{\partial s^3}W+\frac{\partial^3 F}{\partial s^2\,\partial t} \tag{19}$$

Taking the total derivative of $\partial^2 F/\partial s\,\partial t$ with respect to time $t$ and making use of (19), we find

$$\frac{\partial^3 F}{\partial s\,\partial t^2}=\frac{d^2r}{dt^2}-2W\frac{d\delta}{dt}-\delta\frac{dW}{dt}+W^2\frac{\partial^3 F}{\partial s^3} \tag{20}$$

Taking the third total derivative of $F$ with respect to $t$, we can find the expression of $\partial^3 F/\partial t^3$ through $\partial^3 F/\partial s^3$ similar to (13), and from the condition that $d^3Q/dt^3=0$ we can express $\partial^3 Q/\partial t^3$ through $\partial^3 F/\partial s^3$ as in (14).

Thus, one of the third derivatives remains arbitrary. When the value of the one of the third derivatives at the wave-front is given, the other two can be obtained by computation. Let $\partial^3 F/\partial s^3$ be the arbitrary derivative. Differentiating both sides of equation (15) with respect to $s$ and making use of conditions (19) and (20), we shall obtain the ordinary differential equation of the first order for the derivative $\delta$, which it was our object to find and which after substituting $\partial^2 F/\partial s^2 = \delta$ (conditions (12) and (13)) for $\partial^2 F/\partial t^2$ and $\partial^2 F/\partial s\,\partial t$, and $\partial F/\partial s = r$ (condition (11)) for $\partial Q/\partial t$ and $\partial F/\partial t$, will take the general form

$$d\delta = [\delta f_1(t) + f_2(t)]\,dt \tag{21}$$

Here the functions $f_1(t)$ and $f_2(t)$ involve $W$, $U$, $F$ and $r = \partial F/\partial s$ which, as is obvious from the foregoing, can be represented as functions of $s$ or $t$.

For the case where the uniform flow is disturbed by the wave, we get

$$\begin{aligned}\frac{d\delta}{dt} = &-\delta\left(\frac{g}{2}\frac{W-U}{F}Nr+E\right)-r\frac{E}{2(W-U)}\frac{g}{\alpha}\frac{U}{C^2R}\left(1+\right.\\ &\left.+\frac{M(1+\beta)U}{2(W-U)}\right)r+r^2\frac{g}{\alpha C\,RF}\left\{\left(\frac{3}{4}N-2\right)U-W+\right.\\ &\left.+\frac{UM(1+\beta)}{W-U}\left(2W-\frac{9}{8}NU\right)-\frac{U^2}{2(W-U)}\left[M^2(1+\beta)^2-F(1+\beta)\frac{dM}{dF}\right]\right\}+\\ &+r^3\frac{W-U}{F^2}\left[\frac{3}{4}-\frac{F}{B}\frac{dB}{dF}-\frac{3}{4}\frac{F^2}{B^2}\left(\frac{dB}{dF}\right)^2+\frac{1}{2}\frac{F^2}{B}\frac{d^2B}{dF^2}\right]\end{aligned} \tag{22}$$

The investigation of the expressions (15) and (22) will be reported elsewhere.

Equations to compute derivatives of higher orders can be obtained in a similar manner.

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REFERENCES

[1] De Saint-Venant, C. R., **73**, 147, 237 (1871). [2] Kleitz, Ann. des Ponts et Chaussées, 5 série, 8, Mém. T. XIV, p. 133 (1877). [3] С. А. Христианович, Сборн. Некоторые новые вопросы механики сплошной среды, М., 1938. [5] Б. А. Бахметев, О неравномерном движении жидкости в открытом русле, 1928.

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*PHYSICS*

# INTERCOMBINATIONAL TRANSITIONS IN THE SPECTRA OF COMPLEX MOLECULES

By V. L. HERMAN

*(Communicated by S. I. Vavilov, Member of the Academy, 30. IX. 1944)*

The spin disturbance in many complex molecules and heavy atoms cannot be considered small, as is the case in usual atoms and molecules. When it comes into action, the intercombinational forbiddance precluding transitions ($S \rightarrow S'$, $S \neq S'$) between levels with different resultant spins, is known to be removed.

Since, however, the symmetry forbiddance holds good in these cases just the same, the removal of the intercombinational forbiddance cannot by any means always result in the appearance of new types of electronic transitions, differing from the ones usually possible for a fixed $S$.

For them to appear, it is evidently necessary for permissible levels [compare(1)] in the molecules with a given symmetry group and a given number of electrons responsible for the molecular binding which are in states with different resultant spins $S'$ and $S$ ($S \neq S'$), to differ.

Once we have found out when this is the case, we are in a position to determine in which cases to expect removal of the intercombinational forbiddance to result in the appearance of new types of electron levels.

Let N be the number of electrons responsible for bonds inside the molecule (*e. g.* for benzene $C_6H_6$, $N=6$); and $S$, the resulting spin.

In our further reasoning we shall have to know the character $\chi(P_S(C))$ of the permutation $P$, which corresponds to the element of class $C$ of the point symmetry group of the molecule having the spin $S$. This can de determined as the coefficient of $x$ to the power of $k = {}^1/_2 N - S$ in the following generating function ([2],[3]) (compare ([1])):

$$(-1)^{N-\rho}(1-x)\prod_{l=1}^{\rho}(1+x^l)^{j_l} = \sum_k \chi^{(C)}(P_S(C))\,x^k \qquad (1)$$

where $j_l$ is the number of $l$-termed ($l = 1, 2, \ldots, N$) cycles ($j_1 + 2j_2 + \ldots + Nj_N = N$), corresponding to the permutation $P(C)$, and $\rho = \sum_l j_l$ is their total number.

Multiplying the right and left sides of this equation by $\frac{h_c}{h}\chi_i(C)$, where $h$ is the total number of elements in the symmetry group of the molecule; $h_c$, the number of them belonging to class $C$; and $\chi_i(C)$, the character corresponding to the $i$-th irreducible representation of the group (tables for their de-

termination are given in Wigner's paper ([4])), and taking the sum over all classes of $C$ we get:

$$\sum_c \frac{h_c}{h}\chi_i(C)(-1)^{N-\rho}(1-x)\prod_{l=1}^{\rho}(1+x^l)^{j_l}=\sum_k a_i^k x^k \tag{2}$$

Equation (2) is a reducing function for the values

$$a_i^{k=1/2N-S}={}^1/_h\sum_c h_c\chi(P_S(C))\chi_i(C),$$

which immediately give the number of $\Gamma_i$ type* levels corresponding to a state with a resultant spin $S(k={}^1/_2 N-S)$.

Now suppose we are interested in the intercombinational transition $S\rightarrow S'$.

Evidently, if $a_i^{1/2N-S}$ becomes zero for the same types of levels $\Gamma_i$ (or for the same irreducible representation numbers) as $a_i^{1/2N-S'}$ $(S\neq S')$, then even if the intercombinational forbiddance is removed, the appearance of new types of electronic transitions (forbidden for transitions with a fixed $S$) is impossible**.

The values $a_i^{k={}^1/_2N-S}$ from (2) can be written in explicit form as functions of the numbers $j_t$ and $\chi_i(C)$.

The state with the greatest spin possible $S={}^1/_2 N$ $(k=0)$ has the simplest expression:

$$a_i^{k=0}=\sum_c\frac{h_c}{h}(-1)^{N-\rho}\chi_i(C)$$

analogously

$$S={}^1/_2N-1,\ a_i^{k=1}=\sum_c\frac{h_c}{h}(-1)^{N-\rho}\chi_i(C)(j_1-1)$$

$$S=\frac{1}{2}N-2,\ a_i^{k=2}=\sum_c\frac{h_c}{h}(-1)^{N-\rho}\chi_i(C)\left(\frac{j_1(j_1-3)}{2}+j_3\right)$$

$$S=\frac{1}{2}N-3,\ a_i^{k=3}=\sum_c\frac{h_c}{h}(-1)^{N-\rho}\chi_i(C)\left\{\frac{j_1(j_1-1)(j_1-5)}{6}+j_2(j_1-1)+j_3\right\} \tag{3}$$

$$S=\frac{1}{2}N-4,\ a_i^{k=4}=\sum_c\frac{h_c}{h}(-1)^{N-\rho}\chi_i(C)\left\{j_4+j_3(j_1-1)+\frac{1}{2}j_2(j_2-3)+\right.$$
$$\left.+\frac{1}{2}j_2(j_1-1)(j_1-2)+\frac{1}{24}j_1(j_1-1)(j_1-2)(j_1-7)\right\}$$
$$S=\frac{1}{2}N-5,\ a_i^{k=5}=\sum_c\frac{h_c}{h}(-1)^{N-\rho}\chi_i(C)\left\{j_5+\right.$$
$$\left.+\binom{j_1-1}{5}+(j_1-1)\left[j_4-1+\binom{j_2-1}{2}\right]+j_3\binom{j_1-1}{2}+(j_2-1)\binom{j_1-1}{3}\right\}$$
$$(j_1+2j_2+\ldots+Nj_N=N)$$

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* The symbols used here are the same as those given by Bethe ([6]) for irreducible representations.

** It must be noted that in all these cases we have in mind new types of transitions, and not just new transitions between the levels of the types already existing. These latter cannot be examined further after the group theory method, and require special computation for each separate case.

These formulae are convenient to use when $k$ is small (*i. e.* for comparatively low $N$, or for cases when $S$ is nearly maximum). For large values of $k$ (high $N$, or small $S$) they become very cumbersome. In such cases it is usually more convenient to use (2). In (3) $i$ goes through all the irreducible representation numbers.

In order to illustrate the above, we shall perform the computations for two different molecules which have been well studied spectrally.

1. Benzene. Symmetry $D_{6h} = D_6 \times J$ ($h = 24$), the numbers $j_1, j_2, \ldots . j_N$ equal respectively *, for classes $E$, $\sigma_h$: $j_1 = 6$, and all the rest $j_{l \neq 1} = 0$ ($\rho = 6$); $C_2$, $C_2'$, $i$, $\sigma'$: $j_2 = 3$ ($\rho = 3$); $C_2''$, $\sigma''$: $j_1 = 2$, $j_2 = 2$ ($\rho = 4$); $C_3$, $S_6$: $j_3 = 2$ ($\rho = 2$); $C_6$, $S_3$: $j_6 = 1$ ($\rho = 1$).

All the values necessary for the computation are given in the table.

| | $E$ | $C_2$ | $C_3$ | $C_6$ | $C_2''$ | $C_2'$ | $i$ | $\sigma_h$ | $S_3$ | $S_6$ | $\sigma'$ | $\sigma''$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $h_c$ . . . . . | 1 | 1 | 2 | 2 | 3 | 3 | 1 | 1 | 2 | 2 | 3 | 3 |
| $h_c (1)^{N-\rho} \left\{ \frac{j_1(j_1-1)(j_1-5)}{6} + \right.$ | | | | | | | | | | | | |
| $\left. + j_2(j_2-1) + j_3 \right\}$ . . . | 5 | 3 | 4 | 0 | 3 | 9 | 3 | 5 | 0 | 4 | 9 | 3 |
| $h_c (-1)^{N-\rho} \left\{ \frac{j_1(j_1-3)}{2} + \right.$ | | | | | | | | | | | | |
| $\left. + j_2 \right\}$ . . . . . | 9 | −3 | 0 | 0 | 3 | −9 | −3 | 9 | 0 | 0 | −9 | 3 |
| $\rho_c (-1)^{N-\rho}$ $(j_1-1)$ . . | 5 | 1 | −2 | 2 | 3 | 3 | 1 | 5 | 2 | −2 | 3 | 3 |
| $h_c (-1)^{N-\rho}$ . . . . . | 1 | −1 | 2 | −2 | 3 | −3 | −1 | 1 | −2 | 2 | −3 | 3 |
| $\Gamma_1$ . . . . . | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $\Gamma_2 (p_z)$ . . . . . | 1 | 1 | 1 | 1 | −1 | −1 | 1 | 1 | 1 | 1 | −1 | −1 |
| $\Gamma_3$ . . . . . | 1 | −1 | 1 | −1 | 1 | −1 | 1 | −1 | 1 | −1 | 1 | −1 |
| $\Gamma_4$ . . . . . | 1 | −1 | 1 | −1 | −1 | 1 | 1 | −1 | 1 | −1 | −1 | 1 |
| $\Gamma_5$ . . . . . | 2 | 2 | −1 | −1 | 0 | 0 | 2 | 2 | −1 | −1 | 0 | 0 |
| $\Gamma_6 (p_x, p_y)$ . . . . . | 2 | −2 | −1 | 1 | 0 | 0 | 2 | −2 | −1 | 1 | 0 | 0 |
| $\Gamma_7$ . . . . . | 1 | 1 | 1 | 1 | 1 | 1 | −1 | −1 | −1 | −1 | −1 | −1 |
| $\Gamma_8$ . . . . . | 1 | 1 | 1 | 1 | −1 | −1 | −1 | −1 | −1 | −1 | 1 | 1 |
| $\Gamma_9$ . . . . . | 1 | −1 | 1 | −1 | 1 | −1 | 1 | −1 | −1 | 1 | −1 | 1 |
| $\Gamma_{10}$ . . . . . | 1 | −1 | 1 | −1 | −1 | 1 | −1 | 1 | −1 | 1 | 1 | −1 |
| $\Gamma_{11}$ . . . . . | 2 | 2 | −1 | −1 | 0 | 0 | −2 | 2 | 1 | 1 | 0 | 0 |
| $\Gamma_{12}$ . . . . . | 2 | −2 | −1 | 1 | 0 | 0 | −2 | 2 | 1 | −1 | 0 | 0 |

If we multiply lines I,..., IV by the character $\Gamma_i$ ($i = 1, 2, .., 12$), and along each line, and divide by $h$, we get $a_i^S$, respectively for the states: $S = 0$, 1, 2, 3 ($k = 3, 2, 1, 0$), $i = 1, 2, \ldots, 12$.

For $S = 0$ we get the following singulet levels, which are in conformity with the direct computations of Sklar and others ([7],[8]) for the possible excited spin states:

$$S = 1,\ {}^3\Gamma_{S=1} = {}^3\Gamma_2 + {}^3\Gamma_5 + 2{}^3\Gamma_9 + 2{}^3\Gamma_{12}$$
$$S = 2,\ {}^5\Gamma_{S=2} = {}^5\Gamma_1 + {}^5\Gamma_5 + {}^5\Gamma_{12}$$
$$S = 3,\ {}^7\Gamma_{S=3} = {}^7\Gamma_9$$

For $D_{6h}$ the components of the dipole moment $n = \Sigma\, er$ are transformed $p_z \rightarrow \Gamma_2$, $p_x$, $p_y \rightarrow \Gamma_6$. Hence we find in the usual manner that among the singulet levels transition between levels of the type $\Gamma_5$ ($p_z \neq 0, p_x, p_y = 0$) is permitted.

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* $j_1, j_2, \ldots . j_N$ have, as we know, a simple, visual sense: $j_1$ is the number of points out of $N$ that remain fixed during operation $C$: $2j_2$, the number of them that change places in pairs; $3j_3$, the number that change places in threes, *etc.*; $j_1 + 2j_2 + \ldots . + Nj_N = N$.

When the intercombinational forbiddance is removed, besides the possible transiton of the former type, the appearance of a new transition is possible, of the type $\Gamma_1 \rightarrow \Gamma_2$ ($p_z \neq 0$), which was absent among the singulet transitions permissible from the standpoint of symmetry. This transition has, evidently, been observed experimentally also.

2. $C_{14}H_{10}$. Symmetry $C_{2v}(h=4)$; $E$, $\sigma_h$: $j_1 = 14$ ($\rho = 14$), $j_2 = \ldots = 0$; $C_2$, $\sigma'$: $j_2 = 7$ ($\rho = 7$).

Analogous computations give $a_i^S = a_i^{S'}$. Thus, in this case, even after the intercombinational forbiddance has been removed, no new types of transitions can appear.

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REFERENCES

[1] V. L. Herman, C. R. Acad. Sci. URSS, XLI, No 5 (1943). [2] Frobenius, Sitz.-Ber. d. Berl. Akad., S. 516, § 4 (1900). [3] B. L. van der Waerden, Method von Gruppentheorie in Quantenmechanik, § 30, 1932. [4] E. Wigner, Nachr. Ges. Wiss. Göttingen, 133 (1930). [5] L. Rosenthal and G. M. Murphy, Rev. Mod. Phys., **8**, 317 (1937). [7] H. Bethe, Ann. Phys., **3**, 133 (1929). [7] A. L. Sklar, J. of Chem. Phys., **5**, 669 (1937). [8] H. Sponer, G. Nordheim, and A. Sklar, ibid., **7**, 207 (1939).

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*PHYSICS*

# ON THE DETERMINATION OF NUCLEAR SPIN-FUNCTION SYMMETRY IN A MOLECULE. II

By I. GODNEV

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In an earlier paper (1) the author has put forward a method for determining the symmetry of nuclear spin-functions with respect to group $\mathfrak{R}$, the group of permutations of nuclei effected by the rotation of the molecule. The present paper discusses the use of this method in the general case.

Let a molecule having the symmetry number $\sigma$ contain $n$ identical nuclei, whose spin $s_z$ takes $\alpha$ values. The proposed method consist in developing an $\alpha^n$-dimensional representation $D$ into irreducible representations $B_k$ of a symmetrical group $\mathfrak{S}_n$

$$D = \sum_k b_k B_k \tag{1}$$

which is followed by the development of representations $B_k$ into irreducible representations of the group $\mathfrak{R}$.

In the general case explicit formulae for the coefficients $b_k$ can be found as follows.

The $\alpha^n$-dimensional vector space generated by the nuclear spin-functions of the molecule is transformed linearly into itself by permutation of like nuclei and by unitary transformations $u_\alpha$ of $\alpha$ spin-functions of each nucleus; these unitary transformations form a group whose representation $(u_\alpha)^n$ can be developed (2) into irreducible parts

$$(u_\alpha)^n = \sum_k g_k H_k \tag{2}$$

There is a correspondence between the expansions (1) and (2)*: the multiplicity of the representation $B_k$ in (1) is equal to the dimensionality $N_k$ of the representation $H_k$, and the multiplicity $g_k$ in (2) is equal to the dimensionality $B_k$. Into the equations (1) and (2) with coefficients distinct from zero there enter representations whose *partitio numerorum* contains no more than $\alpha$ terms. On the other hand, for the dimensionality $N_k$ of the representations $H_k$ explicit formulae are available (2,3).

Thus

$$b_k = N_k = \frac{D(h_1, h_2, \ldots, h_\alpha)}{D(\alpha-1, \alpha-2, \ldots, 1, 0)} \tag{3}$$

where the quantities $h_i$ for the representations $B_k$ and $H_k$ of the described *partitio numerorum* $n = (n_1 + n_2 + \ldots + n_\alpha)$ are given by the equalities

* For $\alpha = 2$ see(4), for the general case see (5), for instance, where this correspondence is established for a linear group. The application of this correspondence to the unitary group $u_\alpha$ follows from Weyl's data [(2), p. 252].

$$\left.\begin{aligned} h_1 &= n_1 + (\alpha - 1) \\ h_2 &= n_2 + (\alpha - 2) \\ &\cdots\cdots\cdots \\ h_\alpha &= n_\alpha \end{aligned}\right\} \tag{4}$$

and $D(a_1, a_2, \ldots, a_\alpha)$ denotes the determinant

$$D(a_1, a_2, \ldots, a_\alpha) = \begin{vmatrix} a_1^{\alpha-1}, & a_1^{\alpha-2} \ldots a_1, & 1 \\ a_2^{\alpha-1}, & a_2^{\alpha-2} \ldots a_2 & 1 \\ \cdots\cdots\cdots & & \\ a_\alpha^{\alpha-1}, & a_\alpha^{\alpha-2} \ldots a_\alpha, & 1 \end{vmatrix} \tag{5}$$

The dimensionality $g_k$ of the representation $B_k$ is

$$g_k = \frac{n!\, D(h_1, h_2, \ldots, h_\alpha)}{h_1!\, h_2! \ldots h_\alpha!} \tag{6}$$

Carrying out the development of representations $B_k$ into irreducible representations of the group $\mathfrak{A}$, which is a subgroup of $\mathfrak{S}_n$, and substituting in (1) the results of the development, we obtain the sought-for symmetry of nuclear spin-functions.

By way of example consider the application of the above method to $C_2D_2$. In this case $\sigma = 18$, $n = 6$ and $\alpha = 3$ (the spin $s_z$ takes the values 1, 0, $-1$). The results of the expansion of the representation $D$ by means of formulae (3)—(6) is given in the table.

| Irreducible representation of the group $\mathfrak{S}_n$ | *Partitio numerorum* | Dimensionality | Multiplicity in formula (1) |
|---|---|---|---|
| $B_0$ . . . . . | 6 + 0 | 1 | 28 |
| $B_1$ . . . . . | 5 + 1 | 5 | 35 |
| $B_2$ . . . . . | 4 + 2 | 9 | 27 |
| $B_3$ . . . . . | 3 + 3 | 5 | 10 |
| $B_4$ . . . . . | 3 + 2 + 1 | 16 | 8 |
| $B_5$ . . . . . | 2 + 2 + 2 | 5 | 1 |
| $B_6$ . . . . . | 4 + 1 + 1 | 10 | 10 |

Reduction of the representations $B_k$ gives

$$\begin{aligned} B_0 &= \Gamma_1 \\ B_1 &= \Gamma_2 + \Gamma_7 + \Gamma_8 \\ B_2 &= \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_7 + \Gamma_8 + \Gamma_9 \\ B_3 &= \Gamma_2 + \Gamma_5 + \Gamma_6 + \Gamma_9 \\ B_4 &= \Gamma_3 = \Gamma_4 + \Gamma_5 + \Gamma_6 + 2\Gamma_7 + 2\Gamma_8 + 2\Gamma_9 \\ B_5 &= \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_9 \\ B_6 &= \Gamma_1 + \Gamma_2 + \Gamma_5 + \Gamma_6 + \Gamma_7 + \Gamma_8 + \Gamma_9 \end{aligned} \tag{7}$$

The characters of the representations $\Gamma_i$ have been computed by Wilson [6]. From (1) and (7) follows

$$D = 66\Gamma_1 + 55\Gamma_2 + 36\Gamma_3 + 36\Gamma_4 + 28\Gamma_5 + 28\Gamma_6 + 88\Gamma_7 + 88\Gamma_8 + 64\Gamma_9 \tag{8}$$

Symmetry (8) coincides with the results obtained by computing matrix traces and having recourse to direct reduction (6).

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REFERENCES

[1] I. Godnev, C. R. Acad. Sci. URSS, XLIII, 202 (1944). [2] H. Weyl, Gruppentheorie und Quantenmechanik, 2. Aufl., Kap. V, 1931. [3] H. Weyl, Math. Z., **23**, 271 (1925). [4] B. L. van der Waerden, Method von Gruppentheorie in Quantenmechanik, § 30, 1932. [5] B. L. van der Waerden, Mathem. Ann., **104**, 92 (1930). [6] E. B. Wilson, J. Chem. Phys., **6**, 740 (1938).

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*BIOPHYSICS*

# THE CURVE OF ABSOLUTE PHOTOPIC SENSITIVITY OF THE EYE IN THE REGION FROM 300 TO 950 mμ

By N. I. PINEGIN

*(Communicated by S. I. Vavilov, Member of the Academy, 11, IX. 1944)*

According to data by Wentworth([1]) photopic vision in the red spectrum sets in at about 670 mμ under threshold conditions. In our experiments concerned with the determination of eye sensitivity in the region 655—950 mμ colour was perceived already in the 655 mμ region in the same way as in the 700—950 mμ region, *viz.* as an unsaturated red. Special studies on adaptation which will be reported in another paper, have also shown that in the region 655—950 mμ we have to do with photopic vision. We can therefore assert that when determining the spectral sensitivity of the eye in the region between 950 and 655 mμ it is photopic sensitivity we have to do with.

It seemed of interest to compare these data with data obtained by the present author when determining absolute photopic sensitivity in the region from 302 to 700 mμ ([2–3]). No direct comparison of these data is possible, however, data for the 655—950 mμ region being obtained with a $9.21 \times 1.23 \cdot 10^{-1}$ mm rectangular retinal image of the observed object, whereas those for the 302—700 mμ region were obtained with a circular $8.8 \cdot 10^{-3}$ mm² image on the retina. It appeared necessary therefore to determine the transition coefficient from the sensitivity level in the former case with the sensitivity level in the case of the latter image.

With this aim in view we undertook special experiments which involved the determination of the eye sensitivity in the region from 700 to 900 mμ, with a square $8.8 \cdot 10^{-3}$ mm² image on the retina; for this purpose the exit slit of the monochromator had to be reduced from $15 \times 0.2$ to $0.155 \times 0.155$ mm.

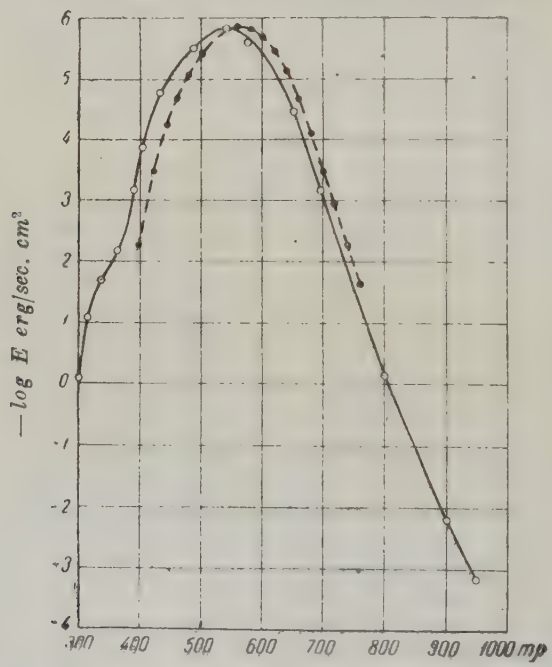
The experiments revealed the existence of two parallel sensitivity levels, corresponding to the two sizes of the monochromator slit. The mean coefficient of transition from the one sensitivity level to the other is 2.71. Supposing that the photopic sensitivity remains constant in the case of transition from a square image on the retina to a circular one, provided both are of equal area, we are brought to assume that the above value of the coefficient holds true for the transition from the sensitivity level with a rectangular image of $9.21 \times 1.23 \cdot 10^{-1}$mm to a sensitivity level with a circular retinal image of $8.8 \cdot 10^{-3}$ mm².

If we compare our data obtained in the region from 655 to 950 mμ with those obtained in the 302—700 mμ region, the former are to be reduced 2.71 times. The table contains average values of the absolute photopic sensitivity of the eye in the form of energetic threshold illumination of the cornea $E$ $\frac{\text{erg}}{\text{sec. cm}^2}$ for the region from 302 to 700 mμ (9 observers) and from 655 to 950 mμ (11 observers), the area of the retinal images being $8.8 \cdot 10^{-3}$ mm² (angular sizes about 20′). The data were obtained under elimination of the chromatic aberration

Absolute Photopic Sensitivity of the Eye in the Region from 302 to 905 mμ
(threshold illumination $E$ on the cornea)

| λ,m | $E$ $\frac{\text{erg}}{\text{sec.cm}^2}$ | $-\log E$ |
|---|---|---|
| 302 | $8.47 \cdot 10^{-1}$ | 0.07 |
| 313 | $8.86 \cdot 10^{-2}$ | 1.05 |
| 334 | $2.13 \cdot 10^{-2}$ | 1.67 |
| 365 | $6.69 \cdot 10^{-3}$ | 2.17 |
| 390 | $6.84 \cdot 10^{-4}$ | 3.16 |
| 404 — 407 | $1.36 \cdot 10^{-4}$ | 3.87 |
| 435 | $1.88 \cdot 10^{-5}$ | 4.73 |
| 491 | $3.35 \cdot 10^{-6}$ | 5.47 |
| 540 | $1.34 \cdot 10^{-6}$ | 5.87 |
| 576 — 579 | $2.74 \cdot 10^{-6}$ | 5.56 |
| 655 | $3.67 \cdot 10^{-5}$ | 4.44 |
| 700 | $4.91 \cdot 10^{-4}$; $6.83 \cdot 10^{-4}$ | 3.31; 3.17 |
| 800 | $7.37 \cdot 10^{-1}$ | 0.13 |
| 910 | 146.05 | — 2.17 |
| 950 | 1504.6 | — 3.18 |

for the eye. The figure shows the curve of the absolute cone sensitivity of the eye in the region from 300 to 950 mμ; along the ordinates are plotted the negative logarithms of the energetic threshold illumination on the cornea. From the table and the curve it is evident that λ=700 mμ is the link point between the data




for the 302—700 mμ region and the data for the 950—655 mμ region. The relation between the mean values of $E_{700\,m\mu}$ does not exceed 1.4, *i. e.* they show but an insignificant discrepancy. It should be pointed out that among the observers three took part both in the experiments with the 302—700 mμ region (1940) and in those with the 655—950 mμ one (1944). With these observers the discrepancy between the mean values of $E_{700 m\mu}$ did not exceed 2.5 per cent. Despite the fact that the experiments of 1940 and 1944 were largely carried out with different observers, the results concerning the link point λ=700 mμ are in fair agreement.

For the sake of comparison the figure contains also the visibility curve according to Gibson and Tyndall ([4]) (dotted line curve); as compared to this curve, our curve is somewhat shifted to the short-wave region of the spectrum: the maximum of our curve corresponds approximately to 550 mμ, while the maximum of Gibson-Tyndall's curve fits within 555 mμ.

The shift of the maximum of the curve of daylight sensitivity may be accounted for by differences in the size of the field of vision. Gibson-Tyndall's curve represents an average of curves obtained with a field of vision of 2 and 3°. In our experiments the field of vision was of about 20′. The existence of a dependence between the shift of the maximum of the curve of daylight sensitivity upon the size of the field of vision and the degree of adaptation has been established by various authors, although there is no full accord among them ([5—10]).

In the ultra-violet, our curve declines appreciably more gently within the region from 365 to 334 mμ; in the infra-red it does so in the region from 700 to 950 mμ.

In concluding let us give here some numerical relations that can be derived from our curve. The daylight (photopic) sensitivity of the eye for 302 mμ is $6 \cdot 10^5$ times lower than for 546 mμ, which approaches the maximum of photopic sensitivity. On the other hand, the sensitivity for 950 mμ is $11 \cdot 10^8$ times lower than for 546 mμ.

The author's sincere thanks are due to S. I. Vavilov, Member of the Academy, and Professor L.N. Gassovsky, for the valuable advice and suggestions made in the course of this work.

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REFERENCES

[1] H. A. Wentworth, Psychol. Monogr., XL, 1930. [2] N. I. Pinegin, C. R. Acad. Sci. URSS, XXX, No. 3 (1941). [3] Н. И. Пинегин, Проблемы физиологической оптики, 2, 4 (1944). [4] K. S. Gibson and E. P. T. Tyndall, U. S. Bur. Stand. Sci. Pap., No. 475 (1923). [5] W. Arndt, Das Licht, 6, 75 (1936). [6] N. T. Fedorov and V. I. Fedorova, C. R. Acad. Sci. URSS, II, No. 9 (1936). [7] A. Dresler, Das Licht, Nr. 5—6,81 (1937). [8] H. Buckley, Philos. Mag., XXIV, No. 165 (1937). [9] J. S. Preston, Proc. Phys. Soc., 50, 398 (1938). [10] N. T. Fedorov, V. I. Fedorova, A. G. Plakhov and L. O. Seletzkaja, J. of Physics, III, No. 1 (1940).

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*TECHNICAL PHYSICS*

# SPECTROSCOPIC DETERMINATION OF CARBON IN IRON AND STEEL

By O. V. BLANK and N. S. SVENTITSKY

*(Communicated by S. I. Vavilov, Member of the Academy, 23. VIII. 1944)*

The most sensitive carbon lines lie in the far ultra-violet part of the spectrum (800—1000 Å)* and are practically inaccessible for modern methods of technical spectroscopy. Those carbon lines which are located in the parts of the spectrum usually used in spectrum analysis, are of comparatively low sensitivity, require large amounts of energy for their excitation, and are almost all overlapped by lines of Fe and other elements present in steel.

The difficulties involved in selecting convenient spectral lines and in exciting them have been responsible for the great number of failures experienced in attempts to evolve spectral methods for the determination of carbon. Although several parers ([1–5]) have been published on this subject, no satisfactory solution of the problem, as far as we know, has been given.

This paper gives the preliminary results of an investigation of two variants of a method of determining carbon spectroscopically.

1. Determination of Carbon by Means of the Spectral Line 4267 Å. The most sensitive line in the visible part of the spectrum is C II 4267 (rather, two inseparable lines: C II 4267.27 and C II 4267.02). These lines appear with the usual condensed spark only in presence of considerable contents of carbon. In order to make the conditions more favourable for the excitement of the carbon spectrum, the induction coil was eliminated entirely from the spark circuit, and the condenser enlarged to 0.09 mF. The spark gap was 0.8 mm, and the high voltage transformer (220/10 000 V) was fed by a current of 9—10 A. Such conditions helped to increase the current density of the discharge, and to raise the intensity of the spectral lines of the ionized atoms. This method of excitation made it possible to detect carbon by its 4267 Å line, with its content as low as 0.3 per cent.

The spectra were photographed with a large Hilger Littrow spectrograph with a glass optic, having a linear dispersion of 5 Å/mm in the 4257 Å region, on orthochrome plates of $400 \times D$ sensitivity. The exposure was 30 sec. for a 0.02 mm slit. The lower electrode was the test-sample on which a flat portion of its surface had been cleaned for this purpose. A copper rod with its end ground to spherical shape, served as the upper electrode.

The C II 4267 line is much diffuse; when the carbon content is about 4 per cent, it takes up over 5 Å of the spectrum. Spectral lines of other elements which may be met with in analysing steels, are also located in this region (Table 1).

* Not to mention the line C I 2478, which is overlapped by the iron lines.

Table 1

| Wave-length, Å | Element | Intensity after Harrison: in the arc | Intensity after Harrison: in the spark | Wave-length, Å | Element | Intensity after Harrison: in the arc | Intensity after Harrison: in the spark |
|---|---|---|---|---|---|---|---|
| 4269.951 | Cr | 40 | 6 | 4267.83 | Fe | 125 | 60 |
| 4269.392 | W | 40 | 30 | 4266.968 | FeI | 70 | 30 |
| 4269.282 | Mo | 30 | 30 | 4265.924 | Mn | 100 | 50 |
| 4268.788 | Cr | 30 | 3 | 4264.74 | FeI | 12 | 2 |
| 4268.758 | Fe | 30 | 10 | 4264.21 | FeI | 35 | 4 |
| 4268.643 | VI | 40 | 20 | 4263.14 | Cr | 125 | 80 |

The distortions these lines cause in the intensity of the carbon lines can be estimated to some extent, since the carbon line is diffuse, while the others are sharp. In this case, instead of the maximum intensity, we took the total integral intensity of the line as the measure of concentration, *i. e.* the area between the contour of the spectral line and a straight line drawn through the minimum point of the background, parallel to the abscissa axis (Fig. 1, shaded portion).

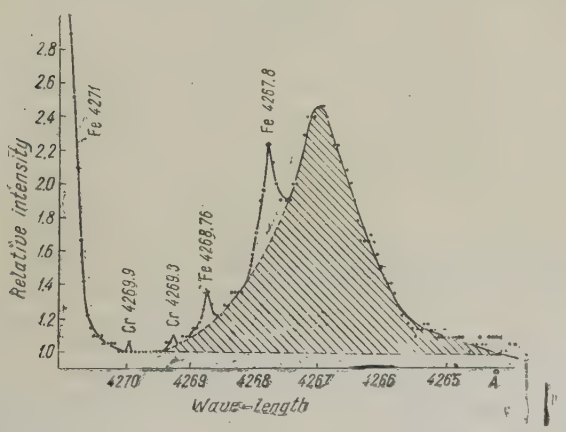


Fig. 1. The contour of the C II 4267 carbon line

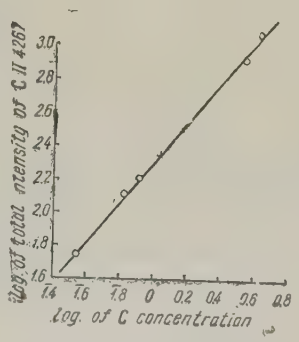


Fig. 2. Calibration graph for the determination of carbon by means of the C II 4267 line

Fig. 1 gives the contour of the C II 4267 line for a carbon content of 4.2 per cent, drawn from the readings of a non-registering GOI (State Optical Institute) photometer (1940 model). Maximum blackening of the Fe 4271 line was selected as the zero reading; each subsequent reading was taken after the carriage and plate had shifted 0.01 mm. The ordinates of the contour represent the intensities of the consecutive points of the section of the spectrum occupied by the carbon line, in relation to the least intensity of the ground in the 4270 Å region *.

If the points of possible superpositions are known, the number of readings can be decreased by five to seven times. The calibration graph, shown in Fig. 2, was plotted from the steel and cast iron samples, whose chemical compositions are given in Table 2. The logarithms of the total relative intensities of the carbon lines were plotted along the ordinate axis, and the logarithms of the carbon contents, along the abscissa axis. The data used in plotting the graph are given in Table 3; these data are the means of the results on eight different photographic plates.

* The use of the spectrum background as an internal standard has been practised in other cases of spectral analysis (7).

Table 2

| No. of sample | Chemical composition, per cent | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C | Mn | Si | Cr | Ni | Mo | V | W |
| 3 | 0.15 | 0.39 | 0.19 | 0.06 | 2.9 | — | — | — |
| 2 | 0.15 | — | — | — | — | — | — | — |
| 11 | 0.35 | 0.39 | 3.06 | 1.62 | 13.0 | 0.24 | — | 1.82 |
| 64 | 0.68 | 0.27 | 0.23 | 4.25 | 0.22 | — | — | 17.44 |
| 84 | 0.81 | 0.31 | 0.25 | 4.85 | 0.09 | 3.32 | 2.31 | — |
| 91 | 1.06 | 0.22 | 0.23 | 4.96 | 0.11 | 3.8 | 2.33 | — |
| 1 | 3.4 | — | — | — | — | — | — | — |
| 39 | 4.2 | 0.75 | 1.07 | 0.96 | 1.24 | 0.16 | — | — |

It is interesting to note that the cast irons and steels are situated on one straight line. Evidently, the individual nature and chemical composition of the

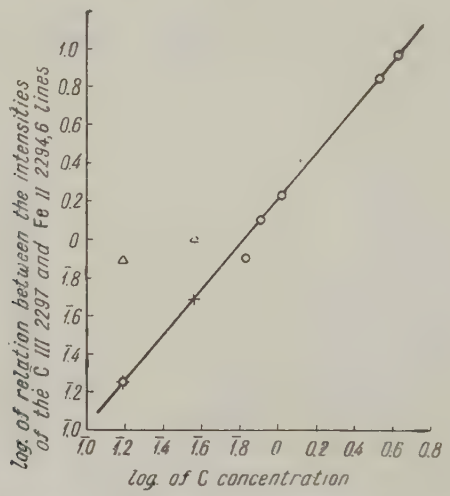


Fig. 3. Calibration graph for the determination of carbon by means of the C III 2297 line

samples have no effect on the relationship between the intensity and the concentration. Roasting was also found to have no effect upon the intensity of the carbon lines; roasting for periods of from 0.5 to 10 minutes did not cause any change in their intensity.

Table 3

| No. of sample | Carbon content, % | log of carbon content | Total relative intensity | log of intensity |
|---|---|---|---|---|
| 11 | 0.35 | $\bar{1}.54$ | 55 | 1.74 |
| 61 | 0.68 | $\bar{1}.83$ | 125 | 2.10 |
| 84 | 0.81 | $\bar{1}.91$ | 160 | 2.20 |
| 91 | 1.06 | 0.02 | 232 | 2.36 |
| 1 | 3.4 | 0.53 | 837 | 2.92 |
| 39 | 4.2 | 0.62 | 1181 | 3.07 |

In order to get an idea as to the reproducibility of these measurements, the relative probable error of an individual determination was calculated from the graph in Fig. 2; for the twenty photographs taken on one plate it was found to be 10 per cent.

2. Determination of Carbon by Means of the Spectral Line 2297 Å. The experiments in the ultra-violet region of the spectrum were performed under the same conditions as those described above, only the glass optic was replaced with a quartz one. The linear dispersion in the 2297 Å region was 2 Å/mm.

The C III 2296.89 line is sharp; under the conditions we used, it is excited quite well enough, and its sensitivity was found to be higher than that of the 4267 line. The superposed line Fe I 2296.92 is no appreciable obstacle even when small contents of carbon are to be determined, but the neighbouring nickel lines (Ni II 2296.5 and Ni II 2297.1), when this element is present in high concentrations, create a considerable background which increases the intensity of the carbon lines. When determining small concentrations of carbon (0.1—0.3 per cent), the presence of one per cent of nickel is enough to cause appreciable error. In order to make allowance for the superposition of the ground from the nickel lines it is necessary to measure this additional ground on both sides of the carbon line, and to subtract its mean intensity from the intensity of the carbon line.

Fig. 3 gives a calibration graph for the determination of carbon by means of its 2297 Å line. This graph was plotted from the samples whose chemical composition is given in Table 2. The logarithms of the intensity ratio of the C III 2297 and Fe II 2294.6 lines are plotted along the ordinate axis, and the logarithms of the carbon content, along the abscissae axis. The points indicated by triangles are for samples containing nickel, when the ground was not subtracted; the crosses show the new positions of these points after subtracting the background made by the nickel lines.

The cast irons and steels are situated, just as before, on one straight line; nor did roasting show any appreciable effect*. The relative probable error of an individual determination from the graph in Fig. 3, calculated from 20 measurements, was 10 per cent.

We take this opportunity to express our deep indebtedness to Professor W. K. Prokofiev for the kind interest he took in our work and for his valuable suggestions.

State Institute of Optics.

Received
23. VIII. 1944.

REFERENCES

[1] F. E. Emery and H. S. Booth, Ind. Eng. Chem. Anal. Ed., 7, 419 (1935). [2] S. Pastore, Metallurgia Italiana, 29, 163 (1937). [3] O. Schliessmann u. K. Zänker, Arch. Eisenhüttenwes., 10, 345 (1937). [4] W. Holzmüller, Z. analyt. Chem., 115, 81 (1938). [5] A. Gatterer u. J. Junkes, Ricerche Spettroscopiche, 1, 24 (1938). [6] G. R. Harrison, Wave-length tables, New York, 1939. [7] S. A. Borovick, C. R. Acad. Sci. URSS, XXVI, 186 (1942).

* It would seem that the deviation of sample No. 61 (Fig. 3) from the straight line should be due to the high content of tungsten (17. 44 per cent) in this sample; if, however, in plotting the calibration graph the Cu II 2294.3 line is taken as the comparison standard, sample No. 61 will be found to fit well into the straight line.

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*PHYSICAL CHEMISTRY*

# THE LIMIT DIAMETER OF A CHARGE OF AMMONIUM NITRATE

By A. F. BELAYEV and J. B. CHARITON

*(Communicated by N. N. Semenov, Member of the Academy, 4. X. 1944)*

For a number of explosives it is known that stable detonation can take place in them only if the diameter of the charge is larger than a certain critical limit value peculiar to each given substance.

It has been pointed out by Rosing(1) and one of the authors of this paper that detonation of any explosive will be stable and sufficiently complete if

$$\tau < T \tag{1}$$

where $\tau$ is the duration of the chemical reaction at the front of the detonation wave, which depends upon the physical-chemical constants; and $T$ is the time in the course of which the pressure of the front of the detonation wave effects the scattering of the reacting substance and the explosion products. This time $T$ should be proportional to the diameter of the charge $d$, since the velocity of scattering cannot depend upon $d$, while the distance to which a particle of the scattered substance must be transposed to cause an equal decrease in pressure of density in the wave front, is proportional to $d$. Hence, instead of (1) we may write

$$\tau < kd \tag{2}$$

for complete detonation.

If, on the other hand, $\tau > kd$, the substance will be scattered before the chemical change has gone through to completion, and the detonation will die out.

$T$ can be made larger than $\tau$ not only by increasing the diameter of the charge, but also by inclosing it in a casing whose strength and mass will retard scattering of the explosive.

In the paper referred above(1) it was shown that even for so sensitive a substance as nitroglycerine, propagation of detonation cannot be stable if the diameter of the glass tube containing the explosive is less than 2 mm.

We thought it would be of interest to establish the magnitude of the limit diameter for a converse case, *i. e.* for an explosive of low sensitivity which is difficult to detonate. The substance chosen for investigation was ammonium nitrate. There has been a great deal of discussion in literature as to whether ammonium nitrate is to be classed as an explosive. The reason for raising this question and, furthermore, in precisely this form, lies in the somewhat dual behaviour of ammonium nitrate as an explosive.

In some experimental researches on the explosiveness of ammonium nitrate complete detonation has been definitely established for comparatively large charges of the explosive. Furthermore, explosion of ammonium nitrate is known to have been the cause of a number of accidents (2). At the same time, however, it is known to be relatively difficult to cause detonation in the nitrate, and that this detonation has a high tendency to die out; under certain conditions it is altogether impossible to effect stable detonation in the nitrate.

On the basis of his experiments Aufschläger ([3]) came to the conclusion that under favourable conditions (big charge, large diameter, sturdy casing) stable detonation can be propagated in ammonium nitrate. Unfortunately, Aufschläger's experiments on which he bases his conclusion are not sufficiently systematic and do not give single-valued results. Scherrick, on the basis of his experiments ([2]) (published after Aufschläger's), arrives at a somewhat different conclusion. He considers that detonation of ammonium nitrate is due to induction of the detonation wave from the detonator. Such a wave spreads through the nitrate charge with ever diminishing velocity and intensity. The distance to which the wave may spread, depends upon the velocity and intensity of the induced wave and upon the strength of the charge casing. It must be said that until recently this opinion, according to which damping of the detonation in the nitrate was absolutely bound to occur, was quite common. It was shared, among others, by the prominent American expert Munroe([2]), who assumed that Aufschläger's statement mentioned above was connected with the fact that he employed an initiator of exceptional power. Then, in some papers (also of a later date than Aufschläger's) it has been stated that the explosive capacity of ammonium nitrate is due entirely to the presence of organic impurities in the nitrate.

Taking into consideration the general condition for stability of detonation formulated above, one should expect detonation of ammonium nitrate to be stable only when the time of scattering is sufficiently great, *i. e.* when the diameter of the charge is large, or, if it is enclosed in a very strong heavy casing. It may be assumed that the extremely abrupt damping of detonation in ammonium nitrate established in some experiments is due chiefly to the fact that these experiments were carried out with charges whose diameter was less than the limit diameter.

One of us in collaboration with E. V. Rdultovskaya carried out a series of experiments with the purpose of determining the stability of the detonation of ammonium nitrate for various charge diameters. These experiments were:

1) to establish definitely whether it is possible to effect stable detonation of ammonium nitrate when the charge is sufficiently large without using a strong or heavy casing nor a powerful initiator, and

2) to establish, for definite conditions, the limit charge diameter for ammonium nitrate.

In our experiments dry powdered nitrate with a density of 0.7—0.8 g/cm$^3$ was packed into thin-walled glass or card-board casings of varying diameters. Initiation was effected with a mixture of 3 per cent TNT and 97 per cent ammonium nitrate. The initiating mixture occupied the upper 10 cm of the casing and in its turn was set off by an electric detonator.

Ammonium nitrate would not detonate without a strong casing directly from the capsule detonator. However, the mixture we employed as an initiator, being very similar to pure ammonium nitrate in its heat of explosion and other explosive properties, can under no circumstances be regarded as a «powerful» initiator.

The experiments were carried out both in an explosion chamber with relatively short charges, the entire course of the detonation being recorded by photographing on a moving film, and under field conditions with relatively big charges of considerable length.

In those cases where the charge diameter in our experiments was greater than 80—100 mm, we observed (and registered photographically) quite stable, non-damping detonation of the ammonium nitrate. The detonation velocity, in a number of cases, even increased somewhat as the explosion spread. When the diameter was less than 80—100 mm, the detonation damped, and so embraced only the part of the nitrate adjacent to the initiator; the rest of the nitrate was scattered or even remained in place. The smaller the diameter of the charge, the more abrupt was the damping of the detonation. From our experiments it follows that the limit diameter at which stable detonation of ammonium nitrate can occur (outside of a strong thick-walled casing) is 80—100 mm (it must be empha-

sized that this is for a nitrate with a density of 0.7—0.8). It is natural, therefore, that Parisot[5], for example, should have observed the detonation of ammonium nitrate to damp in his experiments, since he worked with charges about 20 mm in diameter.

A heavy casing decreases the limit charge diameter for ammonium nitrate, as may have been expected from the considerations at the beginning of this paper. In an aqueous or a thick concrete casing it is about 35—40 mm.

All the results obtained, therefore, are in full conformity with the general considerations put forward at the beginning of the paper.

As a result of the experiments carried out it may be affirmed that, as regards stability of detonation, ammonium nitrate does not differ in principle from other explosives, and is not anything unique. The opinion that only «induced» unstable detonation can spread through the nitrate is incorrect. This term, if it may be used at all, is applicable only for diameters smaller than the limit one, and not only in the case of ammonium nitrate, but also in the case of any explosive, if the diameter of the charge is less than the limit diameter for that substance.

Of course, as regards stability of detonation, there is quite a difference between ammonium nitrate and such substances, say, as TNT, tetril, *etc.* But this difference is only in the limit diameter, which is about 5—10 mm for the latter, in contrast to 80—100 mm for the nitrate.

Thus, in the case of ammonium nitrate (without a strong casing) abrupt damping of the detonation is observed at a diameter, say, of 30 mm. With TNT, on the other hand, the same phenomenon is observed if the diameter of the charge (without a casing) is about 3—5 mm.

In the case of an explosive mixture with a still smaller heat of explosion than ammonium nitrate (for example, a mixture of ammonium nitrate with some inert substance), the reaction time should be greater than the reaction time of ammonium nitrate, and, accordingly, stable detonation of such a mixture will occur only at charge diameters considerably greater than the limit diameter for ammonium nitrate.

The actual values of the limit diameters for such mixtures can be established only experimentally.

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REFERENCES

[1] V. Rosing and J. Chariton, C. R. Acad. Sci. URSS, XXVI, 360 (1940). [2] Ch. E. Munroe, Chem. Met. Eng., **26**, 535 (1921). [3] R. Aufschläger, Z. Ges. Schiess. u. Spr., **18**, 117 (1923); Chem. Met. Eng., **31**, 611 (1924). [4] F. Scherrick, Army Ordnance, **4**, 329, 395 (1924). [5] A. Parisot, Mém. Art. France, **18**, 3 f. (1939).

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*PHYSICAL CHEMISTRY*

# A NEEDLE PROFILOMETER STUDY OF THE OILINESS OF LUBRICANTS

By B. DERJAGUIN and E. PICHUGUIN

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The tendency of lubricants to form a polymolecular boundary film on metal surfaces is usually regarded as a cause of their oiliness. This film, owing to its anomalous properties, which differ from those of the bulk liquid, reduces the friction of rubbing surfaces and decreases their wear, independently of its viscosity. The author of this conception of boundary films, Hardy([1]), advanced the hypothesis that a polymolecular liquid film in a narrow gap between two solid surfaces may develop a pressure that tends to push the surfaces apart. Later the existence of such a pressure, known as the disjoining or wedging pressure, which decreases as the width of the interstice grows, was definitely established ([2]) in oils and for a number of hydrocarbons. In fact, for gaps about $10^{-5}$ cm wide pressures were observed of the order of g/cm$^2$.

It still remained unclear, however, how the disjoining pressure varied with the velocity when the surfaces began to slip in relation to one another, and whether the lubricating film would stay polymolecular at the very high pressures developed in the rubbing parts of machines, especially when their surfaces are rough([3]).

To answer these questions and to estimate the thickness of the lubricating film for the case of kinetic friction between rough surfaces, we evolved the following method based upon the use of a needle profilometer, of one or another type; in the present work we used the Abbot diamond needle profilometer. The method consists in determining the apparent decrease in roughness which results when the metal surface is covered with a layer of the oil being tested. If $\delta_0$ is the mean square height of the protuberances on the surface of a metal before oiling, and $\delta$, after oiling, then the expected effect is characterized by the difference $\Delta = \delta_0 - \delta$. For unoily liquids incapable of forming a boundary film with disjoining action, $\Delta$ should be zero, which is actually the case for non-polar vaseline oil (see table and Fig. 2). Oily liquids, on the other hand, may be expected to exhibit a positive effect.

Let $AA_1$ (Fig. 1) represent the profile of a surface. Then if the boundary lubricating films under the diamond needle point were of the same thickness throughout it would merely shift the trajectory traced by the latter upwards into a position parallel to the trajectory for the dry surface, practically without changing its shape. In this case $\Delta$ would obviously be close to zero. However, in actual fact it should be expected that over the protuberances the pressure of the diamond should cause it to pierce the film to a greater extent than at the points of depression, and it will be counterbalanced by the disjoining action of the latter at small-

er thickness. As a result, the trajectory traced by the diamond point, whose positions are indicated by the dotted line, is distorted, and assumes a more sloping shape $BB_1$.

Thus, obviously, $\delta$ will be less than $\delta_0$, which gives rise to a «Δ-effect».

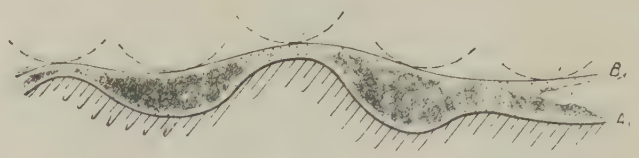


Fig. 1

Measurements of the mean square height of the protuberances were carried out under the following conditions: velocity of slip of needle over the surface of the metal 25 mm/sec.; needle pressure, about 0.1 g; and radius of curvature of the diamond point, 12 μ. The metal surfaces used were made of untempered carbon steel, polished on a polishing lathe. The surface of the plate was cleaned by washing with a highly volatile solvent. In order to exclude the influence of chance variations in roughness over the surface, the following procedure was employed in making the measurements with the profilometer.

The clean, dry metal plate under investigation was placed on a special support, and a needle profilometer calibrated against a roughness standard was so mounted above it that the diamond needle of the instrument touched the metal. The probe was then set in motion. As it moved over the surface, $\delta_0$ was determined for separate portions of the latter from the readings of the galvanometer on the instrument. Then the mean value $\delta_0$ for several adjacent portions of the same sur-

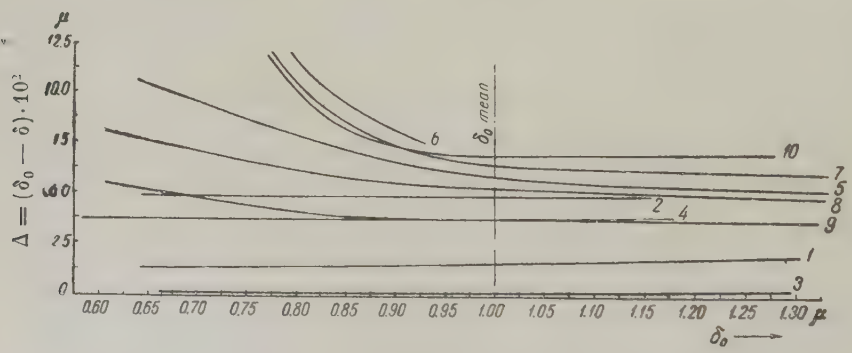


Fig. 2

face was computed. After this the surface of the plate was covered with a layer of the lubricating oil under investigation about 0.1 mm thick, and the whole procedure was repeated. Several measurements were made for each oil not only on different portions of the surface of the same plate, but also on different plates with various degrees of roughness. In the experiments it was found that Δ usually decreases as $\delta_0$ increases. Hence to obtain fully comparable results the oils must be tested on surfaces of exactly the same roughness. However, this requirement is difficult to satisfy; therefore for each oil the apparent decrease in roughness was measured for different values of $\delta_0$ (from 0.5 to 1.5 μ).

A series of $\Delta$ ($\delta_0$) curves for various lubricants is given in Fig. 2. By means of these curves, it was possible to determine the values of Δ (in μ) for the standard value $\delta_0 = 1$ μ. The data obtained are given in the accompanying table.

| Lubricant | Kinematic viscosity in stokes | Oiliness index 100 Δ (in μ) |
|---|---|---|
| Aqueous solution of sodium oleate(1%) | 0.0111 | 1.40 |
| Aqueous solution of alizarine oil (2%) | 0.0133 | 4.70 |
| Vaseline oil | 0.216 | 0.00 |
| Vaseline oil + 5% oleic acid | 0.216 | 3.75 |
| Oleic acid | 0.075 | 5.65 |
| Winter mineral aviation oil + 5% oleic acid | 4.11 | 6.70 |
| Winter mineral aviation oil | 6.71 | 6.20 |
| Castor aviation oil | 10.71 | 5.20 |
| Cylinder mineral oil | 67.6 | 3.75 |
| Surakhan residue aviation oil | 16.0 | 6.70 |

An examination of Fig. 2 and of the table shows that there is a marked difference in the tendency of various oils to «even out» surface roughnesses: this effect for vaseline oil is almost zero, while for good oils $\Delta = 0.05—0.07$ μ. A high «oiliness index» should also be assigned to castor oil and oleic acid; the data

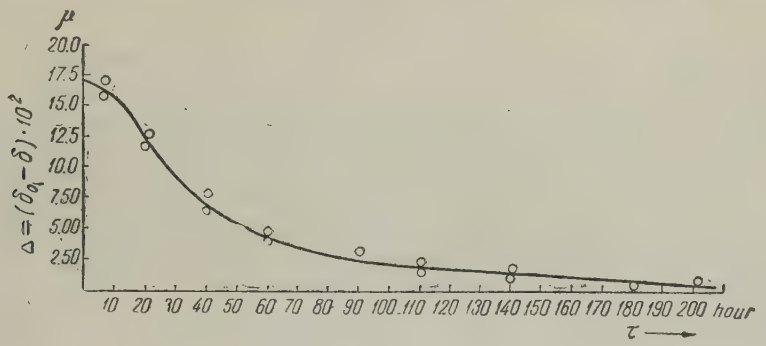


Fig. 3

for a solution of oleic acid in vaseline oil clearly show that small additions of fatty acids cause an increase in oiliness.

In Fig. 3 the index of oiliness of a mineral aviation oil has been plotted as a function of the time τ it has been in a working motor. The graph shows progressive deterioration in oiliness with τ.

It is noteworthy that the method given here is equally applicable to aqueous lubricants *, which can be seen from the data for the 1 per cent aqueous solution of sodium oleate and for the aqueous solution of alizarine oil. The latter, according to our data, should be inferior to medium-grade oils.

In interpreting this effect, we must first of all rule out any attempt to connect it with the viscosity of the oil. This follows from the table, where the viscosity values are given together with the values of Δ. It can be seen that no relation whatsoever exists between Δ and the viscosity. Especially illustrative in this respect is a comparison of the data for cylinder oil and winter aviation oil; notwithstanding the fact that cylinder oil is ten times more viscous than winter aviation oil, it is less effective in «evening out» the surface roughness than the latter. Another proof that the Δ-effect is independent of the viscosity, may be obtained from a study of the influence of the velocity, $v$, of the needle over the surface Δ. It was found that in the velocity interval investigated (from 5 to 60 mm/sec.) Δ does not depend upon $v$, which is evidence against the possible influence of the viscosity.

To explain the Δ-effect it must be assumed that an oil film $10^{-5}$ cm thick between slipping surfaces is capable of developing quite appreciable specific pressures $p$. The order of $p$ may be estimated by assuming that $p$ decreases with the thick-

* We extend our thanks to N. N. Petrova for kindly furnishing us with these oils.

ness $h$, according to the law $p = ah^{-n}$, and applying the formula for the force of interaction $P$ between a plane surface and a sphere(4) of radius $r$, separated by a gap $h$:

$$P = \pi r \int_h^\infty p(h)\, dh$$

Integrating we get

$$P = \frac{\pi r a}{n-1} h^{-n+1} = \frac{\pi r h}{n-1} p(h)$$

and hence

$$p(h) = \frac{n-1}{\pi} \frac{P}{rh}$$

Assuming that $P = 0.1$ g, $r = 10^{-3}$ cm, $h = 5 \cdot 10^{-6}$ cm, and $n = 3$, we get:

$$p(h) \approx 10 \text{ kg/cm}^2$$

These pressures are of a much greater order than the values of the «static» disjoining action.

When the oil film under the diamond point becomes thinner, for example, $10^{-6}$ cm, the counter-pressure it develops should increase to $5 \cdot 10^4$ kg/cm$^2$, and higher. At these pressures, however, it is necessary to alter the method of calculation, owing to elastic deformation of the metal surface in the interstice.

Hence we see that the pressure increases abruptly upon passing over from static to kinetic conditions (cf.(3)), which sheds new light on the principles underlying the oiliness of lubricants.

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REFERENCES

[1] W. Hardy, Phil. Trans. (A), **230**, 1 (1931). [2] B. Derjaguin and E. Obukhov, Acta Phys. Chim. URSS, **5**, 1 (1936); B. Derjaguin and M. Kussakov, Bull. Acad. Sci. URSS, sér. chim., No. 5, 741 (1936); No. 5, 1119 (1937); Acta Phys. Chim. URSS, **10**, 25 (1939); **10**, 153 (1939); C. R. Acad. Sci. URSS, XXIII, 671 (1939). [3] O. Beeck, J. Givens and A. Smith, Proc. Roy. Soc. London (A), **177**, 90 (1940). [5] B. Derjaguin, Koll. Z., **69**, 155 (1934); ЖФХ, 6, 1306 (1935).

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*PHYSICAL CHEMISTRY*

# ENTROPIES OF CRYSTALS AT INFINITELY HIGH PRESSURES

By A. F. KAPUSTINSKY, Corresponding Member of the Academy

Classical thermodynamics is based on two principles. The first is the most general; the second is limited, in its applications, to statistics. In 1906 Nernst added a third law known as the Nernst «heat theorem», whose limitations were more precisely formulated by Planck and later by Lewis and Gibson. The heat theorem deals with changes in the properties of pure bodies in the condensed state as the temperature falls to zero, and makes it possible to estimate the absolute entropies of pure crystals. Various opinions have been expressed regarding the value of this new law, some investigators, like Simon, coming out with unquestionable recognition of this law, others, such as Fawler and Stern, with diametrically opposite views; but notwithstanding unceasing discussion, the third law may be regarded as having firmly entered into the system of modern chemical thermodynamics([1]).

The effect of increase in pressure on the entropy resembles to a certain extent the effect of decrease in temperature. An analysis of this original symmetry between pressure and temperature has been undertaken by a number of investigators([2-6]), who have thoroughly discussed the problem and have thus prepared the grounds for broader generalizations.

In this paper we set forth some new formulations based on a study of the effect of the decrease in volume during isothermal compression upon the thermodynamic properties. In such a study the logical symmetry between the volume and the temperature which, unlike the pressure, are always positive, becomes especially manifest.

According to the first principle of thermodynamics,

$$dQ = ldv + c_v dT \tag{1}$$

where $l$ is the latent heat of change in volume at constant temperature; $l = (\partial Q/\partial v)_T$. Dividing (1) by $T$ we get the change in entropy:

$$dS = \frac{dQ}{T} = \frac{l}{T}\,dv + \frac{c_v}{T}\,dT \tag{2}$$

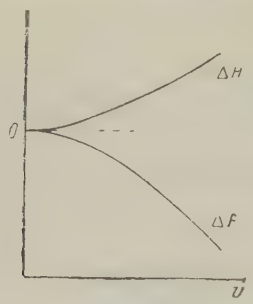
On the other hand, from the definition of the entropy as a function of state *viz.* $S = f(v, T)$, we know that:

$$dS = \left(\frac{\partial S}{\partial v}\right)_T dv + \left(\frac{\partial S}{\partial t}\right)_v dT \tag{3}$$

Equating the coefficients of the differential $dv$ in (2) and (3) $l = T\left(\frac{\partial S}{\partial v}\right)_T$ and comparing this with the Clausius-Klapeyron equations $l = T\left(\frac{dp}{dT}\right)$, we find

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \tag{4}$$

This general expression still tells us nothing about the direction of the change in entropy with the volume. However, as a broad empirical generalization, it may be stated that all pure condensed bodies (with the exception of three or four which are subject to special discussion) expand upon heating, or, upon heating isochorically, increase their pressure.




$$\text{If } \left(\frac{dp}{dt}\right)_v > 0, \quad \text{then } \left(\frac{dS}{dv}\right)_T > 0 \tag{5}$$

Thus, experiment tells us that compression of the volume of a body has the same effect on the entropy as cooling.

The changes in the free energy and the heat content with the temperature are, generally speaking, not equal to one another. Nernst formulated his «heat law» in the form of the following postulate:

$$\lim_{T\to 0} \frac{d(\Delta F)}{dT} = \lim_{T\to 0} \frac{d(\Delta H)}{dT} = 0.$$

But the changes in the heat content and the free energy with the volume are also not equal to one another. From the above it may be postulated that only when the volume approaches absolute zero do they become equal. This makes it possible to express the new thermodynamic law, which we will call the volume law, in the following manner:

$$\lim_{v\to 0} \frac{d(\Delta F)}{dv} = \lim_{v\to 0} \frac{d(\Delta H)}{dv} = 0 \tag{6}$$

*i. e.* in the limit *as bodies are compressed to a volume approaching zero, their properties cease to depend upon the latter.* Then, under such conditions, we have a fair agreement with the Berthelot principle that the heat of reaction is a measure of chemical affinity (see figure)

$$\lim_{v\to 0} \Delta F = \Delta H \tag{7}$$

Applying this new postulate, unlike Nernst's, which we have called the volume postulate, we can define a new perpetual motion machine — «perpetual motion of the fourth order», and prove it impossible. As one of the possible lines of approach we shall use the common thermodynamic relationship:

$$F = H - TS.$$

For analysis of compression processes, we differentiate it with respect to the volume

$$\frac{dF}{dv} = \frac{dH}{dv} - T\frac{dS}{dv} - S\frac{dT}{dv}$$

We shall confine ourselves to an isothermal process. When $T = \text{const}$, $S\frac{dT}{dv} = 0$.

Taking into consideration postulates (6) and (7) and the definition of the latent heat of expansion

$$l = \frac{\partial Q}{\partial v} = T\left(\frac{\partial S}{\partial v}\right)_T$$

we find:

$$l = T\left(\frac{\partial S}{\partial v}\right)_T = 0$$

*i. e.*, upon compression to zero volume, when $v \to 0$, the latent heat of expansion $l$ becomes zero. Other deductions analogous to the one that has been given, also lead to the conclusion that the thermodynamic constants are equal to zero. And since one cannot imagine a body devoid of caloric and thermal properties, we thermodynamically arrive to the conclusion that absolute zero volume is unattainable.

*It is impossible to build a machine capable of compressing a body to absolute zero volume.*

By absolute zero we here mean such a state in which the volume-thermodynamic properties of matter, the so-called «co-volume», do not manifest themselves. It should be noted that absolute zero temperature does not mean complete cessation of motion either, but merely absence of heat motion in the particles of the body in question. Moreover, at 0°K the energy of the zero point is retained.

Passing over to an especially important problem, namely that of an experimental basis of the views discussed here, let us turn to an analysis of the isothermal and reversible compression of a body. From the inequalities (5) it can be seen that during such processes the entropy will decrease. Is this decrease infinite or does it tend to a limit, and to what limit, if it does? The very fact that negative volumes are unattainable, already shows that entropy decrease is conceivable only down to a certain limit value. An elementary statistical analysis, based on the Boltzmann expression $S = k \ln w$, permits us to assume that this limit value is zero, for just as a decrease in temperature results, in the limit, in a uniform thermal state for all the particles of a crystal, a state whose probability equals to unity, so does compression result in a limit state of maximum uniformity for the distribution of the particles in space, and since the probability of such a state is equal to unity ($w = 1$), its entropy will be equal to zero ($S = 0$).

However, there is no need of discarding the purely thermodynamical approach used in our treatment for a statistical interpretation. Meagre as the experimental data on the compressibility of crystals are at present, they uphold the views advanced here convincingly enough.

In a paper we have already referred to ([3]), Lewis showed that if we accept the assumption that the entropy is equal to zero at infinitely large pressure, and express the internal pressure $\pi$ in terms of $(dp/dT)_v$, as is usually done in physical chemistry, namely

$$\pi = \frac{3}{2} T\left(\frac{\partial p}{\partial T}\right)_v$$

we arrive at an equation showing the relation between the thermal expansion and the pressure which includes two empirical constants $\alpha$ and $n$, that can be found from the initial values of $dv/dT$ and the entropy:

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{\alpha}{(P + \pi)^{1+n}}$$

The given equation was found to agree with the experimental data of Bridgman, who studied some alkaline metals over a range of pressures up to 15000 atmospheres. This experimental confirmation of the hypothesis that the entropy is equal to zero at infinite compression is convincing, but unfortunately the only one as yet [cf. Bridgman's criticism ([5])].

All this taken together permits us to express along with the common formulation of the third law of thermodynamics, which says that as the temperature approaches absolute zero the entropy of a pure crystalline phase tends to zero, a new postulate of a general nature:

*as a pure crystalline phase is compressed to zero volume, the entropy tends to zero.*

This offers a new method of determining the absolute value of the entropy. Since, in conformity with the above,

$$\lim_{v \to 0} S = 0 \tag{8}$$

then, taking this into account and integrating (5), we get:

$$S = \int_0^v \left(\frac{\partial p}{\partial T}\right)_v dv \tag{9}$$

The fundamental principles of thermodynamics might be expressed as follows.

The first two principles of so-called classical thermodynamics have to do with restrictions in mutual transformations of heat, work and energy. The first, a quantitative restriction, speaks of the indestructibility of energy. The second, which is qualitative, points to a tendency to the most probable state.

The other principles come under the new thermodynamics, which strives to give an absolute estimation of the thermodynamic functions, this having been found possible only for entropy. These are theses concerning the impossibility of «annihilating» the two fundamental thermodynamic properties of matter, namely, a) the temperature and b) the volume. All of them are very simple generalizations of experimental data, and may be expressed through the perpetual motion, a conception commonly used in modern physical chemistry:

1. Perpetual motion of the first kind cannot be achieved. It is impossible to build a machine that operates without expenditure of energy.

2. Perpetual motion of the second kind cannot be achieved. It is impossible to build a machine in which heat can be transformed into work without restriction.

3. Perpetual motion of the third kind cannot be achieved. It is impossible to build a machine capable of cooling a body to absolute zero.

4. *Perpetual motion of the fourth kind cannot be achieved. It is impossible to build a machine capable of compressing a body to absolute zero volume.*

At present there are still very few precise measurements of thermal properties at high pressures. The situation is about the same as it was in 1906 with regard to low temperature measurements, when a new heat law was put forward that stimulated experimental research into heat capacities. We should consider the purpose of this communication achieved, if it stimulated the interest of experimenters in measuring the thermal expansion of bodies at high pressures.

Confirmation of the views advanced here, which are of the nature of thermodynamic postulates, would contribute to the development of theoretical geochemistry and geophysics, of high-pressure chemical technology, and of the theory of interatomic binding in crystals. At the same time the limitations to which the «volume law» discussed here is subject, might also be defined. Both confirmation of these new views and criticism of them, leading to rational limitations, are equally in need of increased experimental research in the field of high pressures.

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REFERENCES

[1] H. Taylor and S. Glasstone, A Treatise on Physical Chemistry, I, London, 1942. [2] M. Polányi, Verh. deutsch. physik. Ges., **15**, 156 (1913). [3] G. N. Lewis, Z. physik. Chem., **130**, 532 (1927). [4] E. Eastman, Chem. Rev., **18**, No. 2, 257 (1936). [5] P. Bridgman, Rev. Mod. Phys., **7**, 1 (1935). [6] А. Капустинский, Сборник АН СССР акад. Вернадскому, I, 47, 1936.

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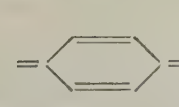
*PHYSICAL CHEMISTRY*

# THE ENERGY OF QUINOID FORMS

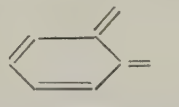
By A. J. NAMIOT, M. E. DIATKINA and J. K. SYRKIN, Corresponding Member of the Academy

There are a number of problems concerning the structure of organic compounds, for the solution of which it is essential to know the energy of quinoid forms. This is necessary, for example, for the elucidation of the significance of quinoid forms in such molecules as nitroanilines and nitrophenols, for the estimation of the rôle of benzoid and quinoid forms in dyes, and in order to determine whether certain hydrocarbons, such as Chichibabin's hydrocarbon, *etc.*, are of bi-radical or quinoid structure.

The general opinion is that benzoid forms are energetically considerably more advantageous than quinoid forms. This viewpoint is based on the fact that quinoid forms have only one possible localization of their four double bonds. However, besides the structure with four normal double bonds in the systems (1) and (2)



(1)



(2)

thirteen more structures are possible with one or several lengthened π-bonds.

In order to throw some light upon this problem the authors undertook a calculation of the energy of para- and ortho-quinodimethane, which are models of systems (1) and (2). The computations were carried out according to the Heitler-

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 8/4 | 1/8 | 4/2 | 2/7 | 2/7 | 4/8 | 2/7 | 2/7 | 2/10 | 4/8 | 4/8 | 4/8 | 4/8 | 2/10 |
| 1/8 | 8/16 | 2/10 | 4/8 | 4/8 | 2/10 | 4/14 | 4/14 | 4/14 | 2/10 | 2/10 | 2/10 | 2/10 | 4/14 |
| 4/2 | 2/10 | 8/—8 | 1/8 | 1/8 | 2/4 | 4/8 | 4/8 | 1/8 | 2/7 | 2/7 | 2/7 | 2/7 | 1/8 |
| 2/7 | 4/8 | 1/8 | 8/—8 | 2/4 | 1/8 | 2/10 | 2/10 | 2/10 | 1/8 | 4/8 | 1/8 | 4/2 | 2/10 |
| 2/7 | 4/8 | 1/8 | 2/4 | 8/—8 | 1/8 | 2/10 | 2/10 | 2/10 | 4/8 | 1/8 | 4/2 | 1/8 | 2/10 |
| 4/8 | 2/10 | 2/4 | 1/8 | 1/8 | 8/—8 | 1/8 | 1/8 | 4/8 | 2/10 | 2/10 | 2/10 | 2/10 | 4/8 |
| 2/7 | 4/14 | 4/8 | 2/10 | 2/10 | 1/8 | 8/4 | 2/10 | 2/10 | 1/8 | 4/8 | 4/2 | 1/8 | 2/10 |
| 2/7 | 4/14 | 4/8 | 2/10 | 2/10 | 1/8 | 2/10 | 8/4 | 2/10 | 4/8 | 1/8 | 1/8 | 4/2 | 2/10 |
| 2/10 | 4/14 | 1/8 | 2/10 | 2/10 | 4/8 | 2/10 | 2/10 | 8/4 | 1/8 | 1/8 | 4/8 | 4/8 | 2/10 |
| 4/8 | 2/10 | 2/7 | 1/8 | 4/8 | 2/10 | 1/8 | 4/8 | 1/8 | 8/4 | 2/10 | 2/7 | 2/7 | 4/8 |
| 4/8 | 2/10 | 2/7 | 4/8 | 1/8 | 2/10 | 4/8 | 1/8 | 1/8 | 2/10 | 8/4 | 2/7 | 2/7 | 4/8 |
| 4/8 | 2/10 | 2/7 | 1/8 | 4/2 | 2/10 | 4/2 | 1/8 | 4/8 | 2/7 | 2/7 | 8/—8 | 2/10 | 1/8 |
| 4/8 | 2/10 | 2/7 | 4/2 | 1/8 | 2/10 | 1/8 | 4/2 | 4/8 | 2/7 | 2/7 | 2/10 | 8/—8 | 1/8 |
| 2/10 | 4/14 | 1/8 | 2/10 | 2/10 | 4/8 | 2/10 | 2/10 | 2/10 | 4/8 | 4/8 | 1/8 | 1/8 | 8/4 |

=0

London-Slater-Pauling method[1] (hereafter referred to for brevity as HLSP), taking into account all 14 structures, and according to Hückel's method of molecular orbitals[2] under the usual assumptions of these methods. The secular equation for ortho-quinodimethane, according to the HLSP method, is given on the page 267.

The corresponding secular equation for para-quinodimethane is:

$$
\begin{vmatrix}
8/-8 & 2/4 & 1/2 & 4/-4 & 2/-2 & 4/2 & 2/1 & 4/-4 & 1/2 & 2/1 & 2/1 & 4/-4 & 2/1 & 4/-4 \\
2/4 & 1/16 & 4/8 & 2/10 & 4/8 & 2/4 & 4/14 & 2/4 & 2/4 & 4/2 & 4/14 & 2/4 & 4/2 & 2/-2 \\
1/2 & 4/8 & 8/-8 & 1/2 & 2/4 & 4/2 & 2/4 & 1/2 & 4/2 & 2/4 & 2/4 & 1/2 & 2/4 & 1/2 \\
4/-4 & 2/10 & 1/2 & 8/-8 & 1/2 & 2/1 & 4/8 & 2/1 & 2/1 & 1/2 & 4/8 & 2/1 & 1/2 & 2/-2 \\
2/-2 & 4/8 & 2/4 & 1/2 & 8/-8 & 1/2 & 2/4 & 4/-4 & 1/2 & 2/4 & 2/4 & 4/-4 & 2/4 & 1/2 \\
4/2 & 2/4 & 4/2 & 2/1 & 1/2 & 8/-8 & 1/2 & 2/1 & 2/4 & 4/2 & 4/-4 & 2/1 & 1/2 & 2/1 \\
2/1 & 4/14 & 2/4 & 4/8 & 2/4 & 1/2 & 8/4 & 1/2 & 4/-4 & 2/4 & 2/10 & 4/2 & 2/4 & 1/2 \\
4/-4 & 2/4 & 1/2 & 2/1 & 4/-4 & 2/1 & 1/2 & 8/-8 & 2/1 & 1/2 & 4/2 & 2/-2 & 4/2 & 2/1 \\
4/2 & 2/4 & 4/2 & 2/1 & 1/2 & 2/4 & 4/-4 & 2/1 & 8/-8 & 1/2 & 1/2 & 2/1 & 4/2 & 2/1 \\
2/1 & 4/2 & 2/4 & 1/2 & 2/4 & 4/2 & 2/4 & 1/2 & 1/2 & 8/-8 & 2/4 & 4/2 & 2/-2 & 4/-10 \\
2/1 & 4/14 & 2/4 & 4/8 & 2/4 & 4/-4 & 2/10 & 4/2 & 1/2 & 2/4 & 8/4 & 1/2 & 2/4 & 1/2 \\
4/-4 & 2/4 & 1/2 & 2/1 & 4/-4 & 2/1 & 4/2 & 2/-2 & 2/1 & 4/2 & 1/2 & 8/-8 & 1/2 & 2/1 \\
2/1 & 4/2 & 2/4 & 1/2 & 2/4 & 1/2 & 2/4 & 4/2 & 4/2 & 2/-2 & 2/4 & 1/2 & 8/-8 & 4/-10 \\
4/-4 & 2/-2 & 1/2 & 2/-2 & 1/2 & 2/1 & 1/2 & 2/1 & 2/1 & 4/-10 & 1/2 & 2/1 & 4/-10 & 8/-32
\end{vmatrix} = 0
$$

These equations are in the generally accepted form. In them the numerator is the coefficient of the difference between the coulombic integral $C$ and the energy of the system $\varepsilon$, and the denominator, the coefficient of the exchange integral $\alpha$. Thus, for example, 8/—8 stands for 8 $(C-\varepsilon)-8\ \beta$. The matrix elements were computed after Pauling's graphical method[3], and the equations solved after the James and Coolidge's method[4]. A computation carried out after the molecular orbitals method resulted in the following level values: for ortho-quinodimethane: $C\pm2.19\beta$; $C\pm1.29\beta$; $C\pm1.19\beta$ and $C\pm0.30\beta$; and for para-quinodimethane: $C\pm2.17\ \beta$; $C\pm1.48\ \beta$; $C\pm\beta$ and $C\pm0.31\ \beta$, where $C$ and $\beta$ stand for the coulombic and resonance integrals in the molecular orbital method. Results of computations after both methods are given in the table.

| | Energy values according to HLSP | | Energy values according to Hückel | | $\beta/\alpha$ |
|---|---|---|---|---|---|
| | total | resonance | total | resonance | |
| Ortho-quinodimethane . . | $C+3.04\,\alpha$ | $1.04\,\alpha$ | $C+9.92\,\beta$ | $1.92\,\beta$ | 0.54 |
| Para-quinodimethane . . | $C+3.05\,\alpha$ | $1.05\,\alpha$ | $C+9.94\,\beta$ | $1.94\,\beta$ | 0.54 |

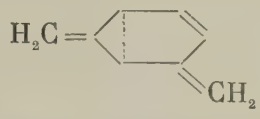
Ortho- and para-quinodimethanes, as the table shows, possess considerable energy. Superposition of all 14 structures results in a high resonance energy. This shows that the quinoid configuration of double bonds is energetically more advantageous than has been thought.

The fact that the quinodimethanes have not been isolated as yet is probably due to their high reactivity.

It is to be noted that the ratio $\beta/\alpha$ is the same in both cases and coincides with its values for other aromatic hydrocarbons ([5]).

It is usually assumed that resonance between the substitution groups of benzene meta-derivatives is impossible. Thus, for example, the internally intraionized structure of meta-nitroaniline cannot be constructed without lengthened $\pi$-bonds. However, slight deviations from additivity are sometimes observed in the

properties of the meta-derivatives (the dipole moment of meta-nitroaniline, the acidity of meta-nitrophenols, *etc.*). This brings up the problem of the energy of the meta-quinoid structure. In the case of hypothetical meta-quinodimethane



14 excited structures are possible. The secular equation for this problem, according to the HLSP method, is as follows:

$$
\begin{vmatrix}
8/4 & 1/2 & 4/2 & 2/4 & 2/4 & 4/8 & 4/2 & 2/7 & 2/1 & 4/8 & 2/-2 & 4/2 & 4/-4 & 2/1 \\
1/2 & 8/4 & 2/4 & 4/2 & 4/8 & 2/4 & 2/7 & 4/2 & 4/8 & 2/1 & 4/2 & 2/-2 & 2/1 & 4/-4 \\
4/2 & 2/4 & 8/4 & 4/8 & 4/8 & 2/4 & 2/4 & 1/2 & 1/2 & 2/4 & 4/-4 & 2/1 & 2/-2 & 1/2 \\
2/4 & 4/2 & 4/8 & 8/4 & 2/4 & 4/8 & 1/2 & 2/4 & 2/4 & 1/2 & 2/4 & 4/-4 & 1/2 & 2/-2 \\
2/4 & 4/8 & 4/8 & 2/4 & 8/4 & 1/2 & 4/8 & 2/1 & 2/7 & 4/-4 & 2/4 & 1/2 & 1/2 & 2/1 \\
4/8 & 2/4 & 2/4 & 4/8 & 1/2 & 8/4 & 1/2 & 4/8 & 4/-4 & 2/7 & 1/2 & 2/4 & 2/1 & 1/2 \\
4/2 & 2/7 & 2/4 & 1/2 & 4/8 & 1/2 & 8/-8 & 1/2 & 4/2 & 2/4 & 1/2 & 2/1 & 2/1 & 1/2 \\
2/7 & 4/2 & 1/2 & 2/4 & 2/1 & 4/8 & 1/2 & 8/-8 & 2/4 & 4/2 & 2/1 & 1/2 & 1/2 & 2/1 \\
2/1 & 4/8 & 1/2 & 2/4 & 2/7 & 4/-4 & 4/2 & 2/4 & 8/-8 & 1/2 & 2/1 & 1/2 & 4/-4 & 2/1 \\
4/8 & 2/1 & 2/4 & 1/2 & 4/-4 & 2/7 & 2/4 & 4/2 & 1/2 & 8/-8 & 1/2 & 2/1 & 2/1 & 4/-4 \\
2/-2 & 4/2 & 4/-4 & 2/4 & 2/4 & 1/2 & 1/2 & 2/1 & 2/1 & 1/2 & 8/-20 & 1/2 & 4/-10 & 2/1 \\
4/2 & 2/-2 & 2/4 & 4/-4 & 1/2 & 2/4 & 2/1 & 1/2 & 1/2 & 2/1 & 1/2 & 4/-20 & 2/1 & 4/-10 \\
4/-4 & 2/1 & 2/-2 & 1/2 & 1/2 & 2/1 & 2/1 & 1/2 & 4/-4 & 2/1 & 4/-10 & 2/1 & 4/-20 & 4/-4 \\
2/1 & 4/-4 & 1/2 & 2/-2 & 2/1 & 1/2 & 1/2 & 2/1 & 2/1 & 4/-4 & 2/1 & 4/-10 & 4/-4 & 4/-20
\end{vmatrix} = 0
$$

The additive energy of one structure amounts to only $C+0.5\ \alpha$, while if all 14 structures are taken into account, the energy is equal to $C+1.41\ \alpha$. This indicates that although meta-quinodimethane is much less stable than the ortho- and para-isomeres, still, owing to a gain in resonance energy, the meta-quinoid forms may be present in small quantities in molecules of the type of meta-nitroaniline.

We also computed meta-quinodimethane after the molecular orbital method. In this case the following level values were obtained: $C\pm2.17\ \beta$; $C\pm1.41\ \beta$; $C\pm1.13\ \beta$, and $C$; $C$. The total energy of the eight electrons amounts to $9.42\ \beta$, *i. e.*, according to this method, meta-quinodimethane is only stightly less stable (by $0.52\ \beta$) than the ortho- and para-isomeres. Similar discrepancies between the two methods were observed by Wheland[5] for free radicals. In this case the resonance energy values computed after the two methods did not agree either. The ratio $\beta/\alpha$ was found to be equal to 0.266. Inasmuch as the level $\varepsilon=C$ is degenerate, meta-quinodimethane may exist, according to the method of molecular orbitals, in the both singlet and triplet forms. It should be pointed out that the method of molecular orbitals is usually in disagreement with the HLSP method in those cases where the first method predicts degeneration of the highest of the occupied levels (cyclobutadiene, cyclooctatetraene and certain free radicals).

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REFERENCES

[1] L. Pauling and G. W. Wheland, J. Chem. Phys., **1**, 362 (1933). [2] E. Hückel, Z. Phys., **76**, 626 (1932). [3] L. Pauling, J. Chem. Phys., **1**, 280 (1933). [4] H. M. James and A. S. Coolidge, J. Chem. Phys., **1**, 825 (1933). [5] G. W. Wheland, J. Chem. Phys., **2**, 474 (1934).

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*GEOLOGY*

# ON THE PRIMARY REGIONAL ZONING OF ORE DEPOSITS OF THE NORTHERN PART OF THE EAST-ASIATIC PACIFIC FOLDED REGION

By M. N. IVANTISHIN

*(Communicated by A. E. Fersman, Member of the Academy, 24. XI. 1944)*

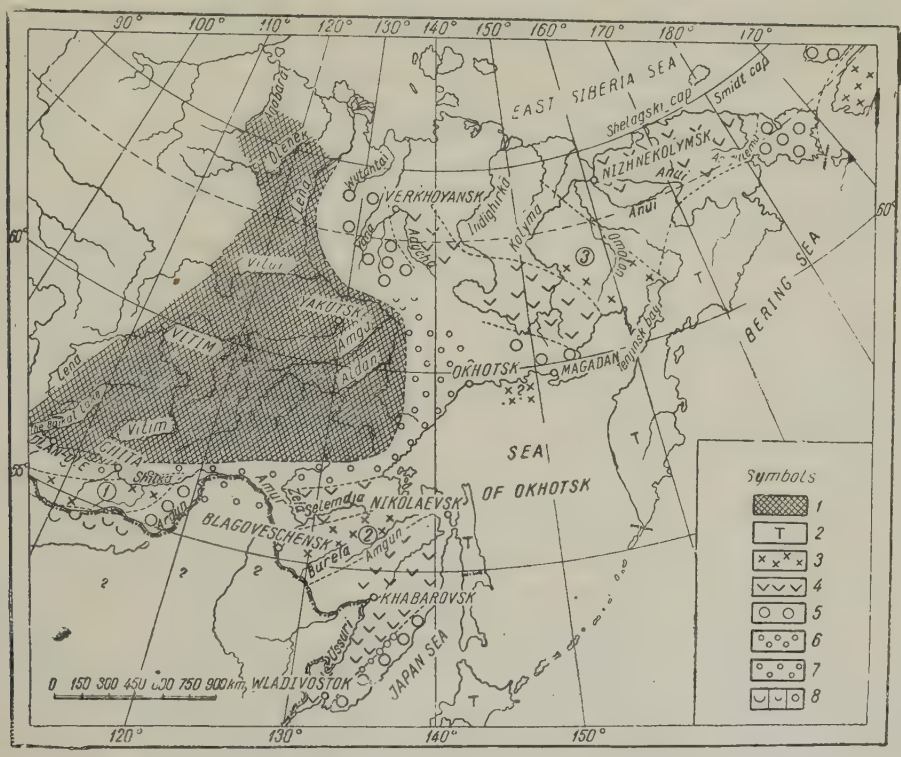
The eastern border of the continent of Asia is encircled by the area of Pacific (Mesozoic) folding, stretching from the Arctic Ocean in the North to the Indian Ocean in the South. The area of development of this folding has been outlined by Arkhangelsky ([1]). The Eastern-Asiatic Pacific folded area (EAPFA) is conventionally subdivided by the present author into two parts: the northern (NEAPFA) and the southern (SEAPFA) one. The NEAPFA is situated chiefly within the USSR. In 1932 Fersman separated within this part of the Soviet Union the Mongol-Okhotsk belt, remarkable for its ore deposits ([2]).

Within the NEAPFA three ore areas may be distinguished at this time: 1) the Transbaikal-Mongolian, 2) the near-Amur-Maritime, and 3) Verkhoyansk-Chukotka area (see figure). These areas display a certain similarity in the distribution of primary ore deposits and a relation between their distribution and the geological macrostructures. In the central portions of the ore areas pass subgeoanticlinal belts, on either side of which subgeosynclinal belts are located. To the subgeoanticlinal belt of the near-Amur-Maritime (Primorie) area is confined the Bureja median massif, which had been separated out by A. D. Arkhangelsky, while to the subgeosynclinal belt of the Verkhoyansk-Chukotka ore area is confined the Kolyma or Alazeya-Yukaghir block. In the eastern Transbaikal in the subgeoanticlinal zone are located the Borshchovochny anticline and the Turga-Borzinsky anticlinorium, separated out by M. M. Tetiaev. An analogous structure is also peculiar to the Alaska, in the central part of which, following a sublatitudinal direction parallel to the general folding of the peninsula, passes the Syuord subgeoanticlinal zone.

Both the subgeoanticlinal and the subgeosynclinal zones are complicated by anticlines and synclines. The central subgeoanticlinal zones of the ore areas of the NEAPFA are distinguished from the subgeosynclinal ones by a more extensive development of exposures of pre-Mesozoic rocks, inclusive of Archaean rocks, as well as by a less intense folding of Upper Mesozoic rocks. The subgeoanticlinal zones of the Transbaikal-Mongolian, near-Amur-Maritime (Primorie) ore areas and of the Alaska are distinguished, as compared to the subgeosynclinal zones, also by a greater abundance of granite intrusions, a greater development of their abyssal facies, a more acid type of the productive granit magma, and a greater development of pegmatites. The central subgeoanticlinal zone of the Verkhoyansk-Chukotka ore area seems to be an exception to this rule.

The principal primary mineralization within the NEAPFA is genetically related to Mesozoic intrusions, including the productive intrusions of the Upper Cretaceous or Lower Tertiary or Sukhote-Alin, the Chukotka and the Alaska.

Considerable difficulties in determining the upper boundary of the productive intrusions are encountered at the subgeoanticlinal zones, in particular, at the near-Amur-Maritime (Primorie) zone, since the Mesozoic deposits occur mainly in synclines, and the granite intrusions, in anticlinal elevations, within which




Scheme of primary regional zoning of ore deposits in the northern part of the East-Asiatic Pacific folded area. Ore areas: **1**, Transbaikal-Mongolian; **2**, near-Amur-Maritime; **3**, Verkhoyansk-Chukotka. Symbols: *1*, platform of Mesozoic folding; *2*, area of Tertiary folding; *3*, central subgeoanticlinal zones (marking associations Mo—W, W—Sn, possibly Ta—Nb; if no intermediate zone, enrichment in Au—East Transbaikal, Alaska); *4*, intermediate zones (main associations: Au—W (in scheelite) As, for the Verkhoyansk-Chukotka area also Sn); *5*, polymetallic subgeosynclinal zones (the possible association is Pb—Sn); *6*, peripheral subgeosynclinal gold-sulphide zone; *7*, tin-polymetallic zone of the near-Amur-Maritime area; *8*, presumed extension of the zone

they are usually in contact with pre-Mesozoic formations. Nevertheless, here too it is possible to observe rare-metal mineralization confined both to the youngest pre-Jurassic granite intrusions (Umalta deposit), and to post-Jurassic granites (see N. I. Baturin) in the basin of the Amgun River. West of the Umalta mine the Jurassic sediments of the Bureia are metamorphosed by the so-called Dimikan massif.

The primary ore deposits of the central subgeoanticlinal zones, on the one hand, and of the peripheral subgeosynclinal zones, on the other, are characterized by high concentrations of certain associations of ore minerals. To the central subgeoanticlinal zone of the Transbaikal-Mongolia ore area correspond high concentrations of Mo, Mo—W, Mo—W—Bi, W—Sn, Li, Be. Widely developed in this zone are granite pegmatites, sometimes carrying columbite, beryl and topaz. The regularity in the distribution of the ore deposits of East Transbaikal has been pointed out by Smirnov(3). No high concentrations of the above ore-forming elements are known within the area of Mesozoic mineralization of the peri-

pheral subgeosynclinal zones; the only exception to this rule is the gold mineralization.

The present author has been the first to point out the geochemical regularities underlying the distribution of the primary ore deposits of the near-Amur-Maritime (Primorie) area ([4]). With the central Bureia subgeoanticlinal zone of the near-Amur-Maritime area are associated high concentrations of Mo, Mo—W, Mo—W—Bi, W—Sn. The presence of molybdenum mineralization in the middle course of the Nonna River on the extension of the Bureia zone, in a SW direction may to a certain extent justify the assumption that the Bureia zone, in particular, may stretch in a SW direction into North Manshuria, and possibly even farther.

In the central subgeosynclinal zone of the Verkhoyansk-Chukotka ore area molybdenum mineralization is known at the Taigonos peninsula at several points on Korkodon River, tin has been found on the Sugoy River, and on the extension of the same zone tin and tungsten are found in the Selennyakha-Indighirka Mts. However, unlike the subgeoanticlinal zones of the Transbaikal-Mongolian and near-Amur-Maritime ore areas, the rigidity of the median massif of the Verkhoyansk-Chukotka area must have been the cause of the poor development of Mesozoic intrusions within the central subgeoanticlinal zone and their more abundant appearance, as well as of the mineralization associated with them, in the adjacent zones; this may have resulted in the intermediate zone, adjoining the Kolyma median massif from the West, becoming enriched in W—Sn ([5–6]).

At the Alaska high concentrations of W, Sn and partly Mo and Li are associated with the central subgeoanticlinal zone.

Confined to the peripheral subgeosynclinal zones of the ore areas of the NEAPFA are mainly polymetallic deposits without gold, or gold-polymetallic (sulphide-gold ore) deposits. Polymetallic deposits without gold are located in East Transbaikal in the eastern near-Argun subgeosynclinal zone; and in the near-Amur-Maritime (Primorie) area, in the eastern Maritime subgeosynclinal peripheral zone. In the Verkhoyansk-Chukotka ore area polymetallic deposits without gold are known in the western peripheral subgeosynclinal zone (Verkhoyansk zone). The eastern peripheral zone of the Chukotka is also characterized by a high concentration of polymetals.

With the western peripheral subgeosynclinal zone of the Transbaikal-Mongolian ore area are associated many sulphide-gold ore deposits, which, according to Smirnov, have many features in common with the polymetallic mineralization of the near-Argun region([4]). Along the strike in a north-eastern direction this zone passes into the peripheral sulphide-gold ore zone of the near-Amur-Maritime area and comprises the western part of the Zeia and Yana-Okhotsk ore-bearing areas. The mineralization of the Allakh-Yuna and Upper Tyrea sulphide-gold-ore area is located on the extension of the western peripheral zone of the near-Amur-Maritime area, and is situated in the southern part of the western peripheral zone of the Verkhoyansk-Chukotka ore area. Farther northward, within the Orulgan Range, this type of mineralization seems to die out, and the highest importance within the peripheral subgeosynclinal zone is acquired by the polymetallic goldless mineralization of the Verkhoyansk zone.

The southern subgeosynclinal zone of the Alaska is well-known for its large gold-polymetallic deposits. In the northern subgeosynclinal zone of the Alaska deposits of polymetals and gold are known in Bird's Mts.; and those of polymetals, in the upper course of the Koyukuk and Chandlar rivers, and at other places.

In the near-Amur-Maritime ore area, between the central Bureia molybdenite-wolframite-cassiterite zone and the peripheral polymetallic and sulphide-gold ore zones pass intermediate zones where gold, scheelite, and arseno-pyrite mineralization is prevalent. The southern part of the eastern Ussuri-Lower Amur, intermediate zone of the near-Amur-Maritime area, is chiefly characterized by arsenopyrite mineralization, while to the northern part of the same area is associated gold, scheelite and arsenopyrite mineralization. The western, Selemdja intermediate zone is mainly a gold-scheelite one, with less significant manifestations of arsenic mineralization. Some portions of the eastern and western

intermediate zones of the Verkhoyansk-Chukotka ore area, in addition to tungsten, arsenic and gold, are also carriers of intensive tin mineralization ([6]).

In the peripheral subgeosynclinal zones, economic tin has been discovered only within the polymetallic zones carrying no gold—the eastern Maritime zone of the near-Amur-Maritime area in the axial part of the Sikhote-Alin Range, and in the Yana zone of the western polymetallic zone of the Verkhoyansk-Chukotka ore area. The tin-polymetallic zone of the Maritime (Primorie) zone is situated in its western portion and is bounded from the West by the Ussuri-Lower Amur intermediate zone ([7]).

The molybdenum mineralization, discovered in the peripheral subgeosynclinal zones, is always found in association with chalcopyrite (copper-molybdenum type, second type, after A. E. Fersman ([8])), occasionally with tourmaline, wolframite being altogether absent. High concentrations of elements of the platinum family are known only within the gold-sulphide subgeosynclinal zones (western part of the near-Amur-Maritime area and the southern Alaska).

As marking ore-forming elements of the primary mineralization of subgeoanticlinal zones and counter-indicators of subgeosynclinal zones in the above ore areas Mo—W, W—Sn and Ta—Nb associations can be considered. The marking elements of subgeosynclinal zones and counter-indicators of subgeoanticlinal zones are high concentrations of the Pb—Zn, Pb—Sn and Mo—Cu associations, as well as of the platinum family elements. Gold, mercury and antimony are no marking elements of mineral zones.

The associations of the marking ore-forming elements, related to granite magma, in the subgeoanticlinal zones of the above considered ore areas, give higher values of vecks, and larger energy levels than the marking elements of subgeosynclinal zones.

Totals of vecks of: A) $Mo + W = 5.34$; $W + Sn = 5.30$; $Ta + Nb = 5.64$. B) $Pb + Zn = 1.92$; $Pb + Sn + 2.80$; $Mo + Cu + 2.82$.

The above relation between the structural and the geochemical factors of the distribution of high concentrations of ore-forming elements is characteristic of the mineral zones of a pure line; it is disturbed in the cases of crossing of marking ore forming elements of subgeosynclinal and subgeoanticlinal zones within one zone. As an example may serve the Tertiary mineralization of the Caucasus, Bolivia, or the Upper Palaeozoic mineralization of South England. The elucidation of the causes of this phenomenon belongs to the future.

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Received
24. XI. 1944.

REFERENCES

[1] А. Д. Архангельский, Геологич. строение и геологич. история СССР, М.—Л., 1941. [2] А. Е. Ферсман, Перспективы распространения полезных ископаемых на территории Союза, Л., 1932. [3] С. С. Смирнов, Перв. Вост.-Сиб. кр. науч.-исслед. съезд, 1, 1932. [4] M. N. Ivantishin, C. R. Acad. Sci. URSS, No. 8—9 (1935). [5] G. L. Padalka, Bull. Acad. Sci. URSS, sér. géol. No. 5 (1939). [6] S. S. Smirnov, ibid., No. 5—6 (1938). [7] М. Н. Ивантишин, Вестн. ДВФ АН СССР, № 33 (1939). [7] А. Е. Ферсман, Геохимия, IV, М.—Л., стр. 185, 1939.

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*MINERALOGY*

# THERMONATRITE IN THE NEAR-KAMA REGION

By A. A. APRODOVA

*(Communicated by W. I. Vernadsky, Member of the Academy, 29. VIII. 1944)*

Thermonatrite has been discovered in the area of the Gorodki oil deposit, located at Verkhne-Chussovskie Gorodki, 70 km north-east of the town of Molotov.

Although the waters of the deposit have been studied both lithologically and chemically since the discovery of oil in 1929, the geochemical conditions still remain obscure.

When studying the lithology of the rocks from well K-7 in the Fofanov-Sychev area of the deposit, the present author discovered amidst Kazan deposits at a depth of 16.20 m a bed of thermonatrite ($Na_2CO_3.H_2O$),1.10 m thick. The recovery of the core within a range of 16.20—18.20 m is 95 per cent. The incomplete recovery of the core was probably due to the dissolution of thermonatrite; its thickness can be brought to 1.20 m.

Macroscopically, thermonatrite is a brownish-grey, breccia-like slightly cavernous rock, contaminated with pelite. Its breccia-like appearance is caused by the presence of irregularly angular white inclusions of pure thermonatrite. Along with this, there occur small (up to 1—3 mm) pebbles of limestone, resembling the limestone overlying the thermonatrite. Upon short exposure to air, the flesh flacture of the brownish-grey rock is covered with a thin white weathering clust. Since the moment of drilling (4.XII.1940) till now an annular crust (2 cm thick) of friable yellowish thermonatrite with soda has been formed on a core with a diameter of 10 cm during 4 years. It is contaminated with clayey and sandy particles, which are contained in a large amount at the base of the bed. The inclusions of white thermonatrite in the weathering crust contain pure soda (10 per cent).

Thermonatrite has a vitreous lustre. Streak, colourless in the white variety and yellowish in the brownish-grey one. Hardness, 1.5—2.0; scratchable with the nail. Specific gravity varies within the range of 1.70 to 1.74. Vegetable remains in the shape of indeterminable small branches and stalks of brownish-fallow colour have been found in the rock. Some of them are charried. An analysis of the pollen made at the Laboratory of the Molotov Oil Combinate («Neftekombinat») by M. A. Sedova revealed the presence of rare spores and pollen, indeterminable with greater precision because of their poor preservation. As to their appearance and state of preservation they are like the pollen found in the Yugov series ($P_2^{kazjug}$) of the region.

From the data of chemical analyses made at the Laboratory of the above-named Combinate (by M. I. Vilenchik) and at the Laboratory of the Department of Physical hemistry of the Molotov State University (V. F. Ust-Kachkintzev), the rock has the following chemical composition:

| Components | Grey thermonatrite | White compact inclusions | Friable white inclusions |
|---|---|---|---|
| Insoluble residue | 8.64 | 0.72 | 0.30 |
| Crystallization and hygroscopic water | 37.76 | 27.10 | 42.28 |
| Na | 22.16 | 31.25 | 24.60 |
| K | 0.03 | 0.07 | 0.04 |
| Ca | 0.56 | 0.01 | 0.12 |
| Mg | 0.02 | none | traces |
| $CO_3$ | 28.04 | 40.50 | 32.08 |
| $HCO_3$ | none | none | none |
| Cl | 0.38 | 0.12 | 0.16 |
| $SO_4$ | traces | traces | traces |
| $R_2O_3$ | 2.09 | indeterm. | indeterm, |
| Total | 99.68 | 99.77 | 99.58 |

The present interesting and rare finding of thermonatrite will open a new page in the study of the chemistry of waters and in the geochemistry of the near-Kama region in general. Alkaline underground waters have thus far been considered alien to the rock complex of the Palaeozoic of the near-Kama region.

It is necessary to trace the outlines of the newly discovered thermonatrite deposit and to study it on a larger scale.

The Central Scientific Research Laboratory
of the Molotov Oil-Combinate.

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*MINERALOGY*

# NEW DATA ON THE REFRACTORINESS OF ARTIK TUFF LAVA

By R. L. PEWZNER

*(Communicated by I. P. Bardin, Member of the Academy, 11. X. 1944)*

The volcanic tuff lava, deposits of which are located in Armenia at an altitude of 1700—2100 m above sea level, has long since been used as building material. This is evidenced by the most ancient ecclesiastical buildings of the 7th and 9th centuries (the Greek and the Kipchag church), which have partly surviving until the present day.

The best explored region of the tuff lava occurrence is located on the southwestern slope of Mt. Alaghez, 22 km of the town of Leninakan, within the villages of Old-Artik, Kipchag and Kachkilas. This explored area of volcanic lava deposits is now widely known under by name of the Artik region.

The Institute of Economic Mineralogy carried out a series of studies on the tuffs of the Artik deposit, dealing with the quality of the tuff and its reserves, and developing methods for an industrial utilization of the Artik tuff as building material. A detailed description of the work is given in the paper of Chisliyev (1). No other cases of practical application of the Artik tuff lava have ever been reported.

The investigations carried out by the present author have for the first time revealed very interesting features concerning the behaviour of the Artik tuff lava under load at high temperatures.

The properties of this lava as revealed by the author make it possible considerably to extend the field of its application as a new substitute for refractory materials applicable within a temperature range up to 1100°. The experimental data obtained by the author under laboratory conditions went to support these conclusions.

Two varieties of Artik tuff lava were investigated: No. 1, light-grey with a pinkish shade; No. 2, dark-grey.

The chemical composition of the specimens tested is given in the table (in per cent).

A microscopic study of specimen No. 1 in an uncalcined condition has shown it to consist of a strongly porous vitreous groundmass, made turbid by finely disseminated iron oxides, occasionally forming small black-coloured accumulations. Near the pores, in the groundmass, a considerable quantity of cristobalite of birefringent form is observed. In this vitreous groundmass minute prisms of plagioclase are present, as well as larger phenocrysts of (a) feldspar-plagioclase, in the form of occasionally strongly melted grains up to $2.5 \times 0.8$ mm in size; (b) fragments of lava mainly consisting of microlites of feldspar and showing rounded outlines, as a result of a partial melting; (c) crystals of pyroxene up to 0.3 mm in size.

| | Specimens | |
|---|---|---|
| | No.1 | No.2 |
| $SiO_2$ . . . | 64.80 | 65.12 |
| $TiO_2$ . . . | 0.42 | 0.27 |
| $Al_2O_3$ . . . | 16.64 | 16.01 |
| $Fe_2O_3$ . . | 4.03 | 3.87 |
| FeO . . . | — | 0.65 |
| MnO . . . | 0.39 | 0.41 |
| CaO . . . | 2.76 | 2.69 |
| MgO . . . | 0.38 | 0.27 |
| $Na_2O$ . . . | 4.87 | 5.12 |
| $K_2O$ . . . | 4.76 | 4.91 |
| $SO_3$ . . . | 0.38 | 0.41 |
| $H_2O$ . . . | 0.57 | 0.24 |
| Total . . . | 100.0 | 99.94 |

The pores are either rounded, isolated, 0.4—0.10 mm in size, or united, of irregular shape and much larger in size.

Specimen No. 2, as to its external appearance in an uncalcined condition (except for its colour) and as to its microstructure, is similar to specimen No. 1, differing from the latter only in the absence of phenocrysts of melted fragments of the rock.

A test for determining the temperature of deformation under load at high temperatures has shown for uncalcined Artik tuff: beginning of deformation, at 1100°; end of deformation, at 1140°.

A microscopic study of specimens subjected to the effect of temperatures up to 1140° has shown:

Specimen No. 1a (*i. e.* specimen No. 1 after calcination), somewhat agglomerated, as to external appearance, more compact. The general nature of the microstructure has been preserved after calcination. Within the vitreous groundmass somewhat less pores are observed, and these are in most cases isolated rather than united. The groundmass is impregnated with very fine iron oxide segregations, black in ordinary light and assuming a red-brown colour upon introducing the upper nicol and the «LAZO» lens. The amount of the vitreous phase is somewhat increased at the expense of partial additional melting of feldspar microlites. Cristobalite, like that in specimen No. 1, is present as a birefringent variety, occasionally pseudomorphs of tridymite (twins) after cristobalite being observed.

Specimen No. 2a (*i. e.* specimen No. 2 after calcination) is similar to specimen No. 2. In the vitreous groundmass, containing birefringent cristobalite near the pores, are seen impregnations of melted pieces of microlitic (feldspar) lava. The porosity changes with a trend towards the formation of isolated rounded pores instead of united ones.

It is also necessary to point out the good thermal resistivity of the Artik tuff lava: specimens removed from the furnace, upon being heated to 1140 , immediately subjected to the action of a profuse jet of cold tap winter, did not show any sign of cracking.

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REFERENCES

[1] Д. Г. Числиев, Тр. ин-та прикл. минералогии, М., 1930.

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*GENETICS*

# A CONTRIBUTION TO THE CHROMOSOME MORPHOLOGY OF HARD WHEAT

By V. PODDUBNAYA-ARNOLDI

*(Communicated by I. I. Schmalhausen, Member of the Academy, 16. I. 1945)*

In the present communication I am dealing with data obtained by me on chromosome morphology of *Triticum durum* subsp. *expansum* v. *melanopus*, *T. durum* subsp. *abyssinicum* v. *arraseita* and *T. durum* subsp. *abyssinicum* v. *gondaricum*. The material has been obtained from the wheat section of the All-Union Institute for Plant Industry. The technique was as follows: after shortening the chromosomes by chilling, the rootlets were fixed with platino-formol, sectioned with the microtome to 16 mμ and stained with Heidenhain's haematoxylin. This method yielded better results with regard to chromosome differentiation than any other method previously applied. Even this method cannot, however, be regarded perfect, as secondary constrictions could not always be observed with the same clearness and constancy. The study was hindered, besides, by the fact that plates with good chromosome arrangement could be found in the *Triticum* species with greatest difficulty. Even with a considerable shortening of the chromosomes I failed to find plates where all the chromosome types showed their differentiation with sufficient clarity and were well arranged.

Drawings of the chromosome plates of different wheat species are found in the works of many students. However, the great majority of them, except for Kagawa, Sarana, Hasegawa, Levitsky, Sizova and Poddubnaya-Arnoldi([1–5]), picture chromosomes as thin, long, more or less bent ribbons, poorly arranged and showing no differentiation.

Kagawa([2]) was the first to discover the differentiation of the wheat chromosomes; he has laid foundation to the study of the morphology of the chromosomes of the different wheat species, including *T. durum*, by using chromosome shortening with the aid of chloralization and fixation of the rootlets with Benda's fixative. Kagawa's works are interesting, aside from the chromosome differentiation in a number of wheat species found by him, because of the general conclusions which were of importance for the problem on the origin of wheat species and their phylogeny. He arrived at a conclusion that, although the 28- and 42-chromosome species are numerically tetraploid and hexaploid, the individual chromosome types are represented here not four and six times, but only in duplicate. Kagawa concluded from this finding that the species of hard and soft wheat had originated not through simple multiplication of the chromosome complements of diploid species (more precisely, *Triticum monococcum*), but by means of crossing species differing in chromosome complements, followed by chromosome duplication, the polyploid wheat species being allopolyploid. Later on Levitsky, Sizova and Pod-

dubnaya-Arnoldi have confirmed and supported in more detail Kagawa's conclusions on the morphological difference between the genomes of wheat species.

Indications to the chromosome morphology of certain wheat species *T. durum* included, although followed by no general conclusions, are to be found in work by Sarana ([5]) and Hasegawa ([1]).

In recommending chilling for making easier the studies of chromosome morphology in cultivated *Gramineae*, Sarana depicts chromosome plates of *T. du-*

Fig. 1. Metaphase from a root tip of *T. durum expansum* v. *melanopus*, ×5000; below, chromosomes possessing appendices, ×5000

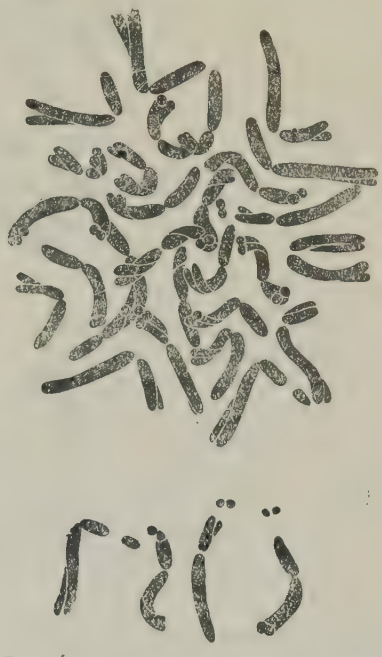

Fig. 2. Metaphase from a root tip of *T. durum abyssinicum* v. *arrasei-a*, ×5000; below, chromosomes possessing appendices, × 5000

*rum* and notes the presence of chromosomes with appendices, differences in chromosome length and in the ratio of the length of their arms. Hasegawa, who has studied the first division of the pollen nucleus in *T. durum*, has discovered median and submedian constrictions, as well as secondary constrictions, separating the appendices in some of them.

All the chromosome types found by me in *T. durum* may be subdivided as follows: 1) chromosomes showing secondary differentiation; 2) chromosomes of different length with more pronounced difference in the sizes of the arms; 3) chromosomes of different length with less pronounced difference in the size of the arms; and 4) chromosomes with almost equal arms, of different length and without secondary differentiation. Among the chromosomes possessing secondary differentiation in *Triticum durum*, as well as in other species of hard and soft wheat, the most characteristic and constantly occurring are those possessing rather large appendices; these chromosomes are usually two pairs in number.

The present paper is not intended to describe and compare complete idiograms of the varieties of *T. durum* enumerated above; I shall deal only with chromosomes possessing appendices, as they are most easily observed and compared to each other. One of the varieties studied by me, namely *T. durum* subsp. *abyssinicum* v. *gondaricum*, appeared to be sharply distinguished from others by having one pair of very anisobrachial chromosomes with appendices, and another pair of very small isobrachial chromosomes similarly possessing appendices. Such small chromosomes with appendices were found neither in the two other varieties

of *T. durum* studied by me nor in other species of hard or soft wheat. In *T. durum expansum* v. *melanopus* and *T. durum abyssinicum* v. *arraseita*, like in other species of hard and soft wheat, the two pairs possessing appendices are large and have sharply unequal arms. My study has thus demonstrated in the various forms

Fig. 3. Metaphase from a root tip of *T. durum abyssinioum* v. *gondaricum*, × 5000; below, chromosomes possessing appendices, × 5000

of *Triticum durum* the existence of clear differences in the organization of the chromosomes possessing appendices, these differences being expressed in a sharp shortening of the one of arms in a pair of these particular chromosomes. The discovery of intraspecific variations has led to a further more detailed study of *T. durum*, especially of its Abyssinian varieties; this work is done by Sizova[6] with the aim of finding out the nature of the intraspecific differences. It is possible that the formation of a pair of small isobrachial chromosomes possessing appendices in *T. durum abyssinicum* v. *gondaricum* was due to translocation and should be interpreted as evidence of structural changes which had taken place in addition to chromosome duplication.

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REFERENCES

[1] N. Hasegawa, Jap. J. Genetics, X, 1 (1934). [2] F. Kagawa, Cellule, 37 (1937). [3] F. Kagawa, J. of College of Agriculture of the Imper. University of Tokyo, X, 2 (1929). [4] G. A. Levitsky, M. A. Sizova, V. A. Poddubnaya-Arnoldi, C. R. Acad. Sci. URSS, XXV, No. 2 (1939). [5] M. Сарана, Вісник прикл. бот., No. 5—6 (1930). [6] M. A. Sizova, C. R. Acad. Sci. URSS, XXV, No. 1 (1939).

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*GENETICS*

# ON THE DIPLOID SPECIES OF YELLOW ALFALFA

By E. N. SINSKAYA

*(Communicated by N. V. Zizin, Member of the Academy, 22. II. 1945)*

The common yellow alfalfa which is widespread in the steppe, woody-steppe and some woody districts of the European Russian plain and Western Siberia is a tetraploid form ($2n=32$). The yellow alfalfa growing in the piedmount meadows of the north-western Caucasus proved to be diploid, having 16 chromosomes at its diploid phase ($2n=16$). A description of this form is given below.

The plants are usually vigorous with a great number of stems, from 50 to 100 cm in length. The branches form with the stem an angle of more than 45°, or nearly a right angle. The shape of the bush varies from the prostrate to the upright one. Foliage profuse. The leaflets are dark-green (not grey), elongated, oval or oval-wedge-like in shape, more often completely naked from top and covered with scarcely noticeable hairs below. The clusters are for the most part large, from 2.5 to 5 cm in length, short-cylindrical or egg-shaped, sometime tufty and less compact as compared to the common forms of *Medicago falcata*. The length of the flowers varies from 7 to 9 cm. The flag is broad, rounded-oval in shape. Petals yellow or yellowish. The beans are quite straight or slightly bent, covered by very short hairs, or nearly naked, easily splitting. The chromosome number is $2n=16$.

The plant is common to the forest glades of the north-western Caucasus, less frequently met on rocks along the Belaya River. Surroundings of Maikop, valleys of the Belaya, Kurdzhipsa, Shuntuk, Kodzhokh, Polkovnitzkaya Balka, Dakha rivers. Surroundings of villages Bezvodnaya, Dakhovskaya, Mostovskaya, Apsheronskaya, Gubskaya, Tzerbelevi Polyani (*ca.* 1000 m above sea level), slopes of the Loganaki mountain range (up to 1800 m above sea level).

The piedmount yellow alfalfa of the north-western Caucasus has been identified by the author as an independent species, *Medicago quasifalcata*, on account of the following data:

1) Although highly polymorphous, *Medicago quasifalcata* species represents a single system of ecotypes connected with one another by gradual intermediate forms composing, on the whole, a definite system of populations having a definite area of distribution.

2) We have never observed such a gradual change in populations of *Medicago quasifalcata*, overlapping the populations of another species, as in Kabardino-Balkaria and Karachai, where populations of tetraploid *M. glutinosa* gradually pass into populations of typical tetraploid *M. falcata*. At the upper boundary of its distribution, *M. quasifalcata* does not come into contact with *M. glutinosa* populations, for the latter are absent there.

3) From North, West, East, and partly from South *Medicago quasifalcata* is surrounded by tetraploid forms of the typical *M. falcata*, from which it is isolated physiologically, for it does not readily cross with them. Although the natural

hybrids between tetraploid and diploid forms are occasionally met with, according to our observations, they are of rare occurrence.

4) *Medicago quasifalcata* differs greatly from all known diploid forms of the yellow alfalfa whose foci of distribution (Daghestan, South Kazakhstan) are rather remote from those of *M. quasifalcata*.

5) *Medicago quasifalcata* is morphologically different from the diploid species of the dark blue alfalfa *M. hemicycla* and *M. coerulea* with which it crosses with great difficulties.

Thus, the yellow piedmount alfalfa, *Medicago quasifalcata*, is a species, well-limited both geographically and physically, although the general habit of the forms of this species is not as different from that of the typical *M. falcata*, as to be safely identified on account of its external characters only. We are facing here a most instructive example of how the cytological method of identification can be applied in taxonomy. The other diploid forms of the yellow alfalfa known are different from *Medicago quasifalcata* and present difficulties in crossing. The percentage of successful crosses is low. The hybrids are sterile. Such forms were found by us in Daghestan and at the Caucasus.

The Daghestan and Kazakhstan diploid yellow alfalfas are similar to each other with respect to their thin stems, narrow leaflets, small clusters and flowers. They are more similar to each other than to the North-Caucasus diploid yellow alfalfa. At the same time the Kazakhstan forms differ from the known Daghestan forms in a number of xeromorphic peculiarities. These are as follows: strong hairiness, the stems are tough; the plant is more vigorous and rough; the clusters are compact, intense yellow (almost orange); the leaflets and beans are hairy, the hairiness makes the whole plant look grey. In the Daghestan diploid plants the stems are slightly upright, the clusters less compact; the petals are somewhat lighter in colour; the leaflets are naked or nearly so, without a grey shade. The plants of these forms look, on the whole, like those of *Medicago hemicycla*. In the Daghestan forms the beans are narrow, naked, slightly bent or crescent, while in the Kazakhstan forms they are short, broader, straight or slightly bent, and grey owing to hairiness.

Thus far no large populations of diploid forms are known from Daghestan and Kazakhstan; but the possibility of their existence is not excluded. Both regions mentioned have been studied in respect to the forms of yellow alfalfa alone, and we unite them into an independent species, *Medicago difalcata*, in a purely provisory way, in order to draw a borderline between them and the well-distinct north-caucasian diploid species, *M. quasifalcata*. It is possible that in the course of further searching work it will be necessary to establish here two or even more species of the eastern yellow alfalfa. And here again, cytology will have recourse to, in order to help in bearing out the hidden species.

The diploid species of yellow alfalfa are of interest from the point of breeding. The yellow diploid alfalfa, widespread on the forest glades of the north-western Caucasus, gives a heavier yield of fodder and is immune against diseases. Kazakhstan diploid forms are resistant to high temperature.

The plant breeder should know, whether he is dealing with a diploid or a tetraploid form of yellow alfalfa. It is a well-known fact that the varieties with an identical chromosome numbers produce hybrids more easily than those having different numbers of chromosomes. And again, diploid forms can be reproduced without spatial isolation, side-by-side with varieties obtained from tetraploid forms of yellow alfalfa.

Received
22. II. 1945.

REFERENCES

[1] Е. Н. Синская, Бот. журн. СССР, **23**, 4 (1938). [2] М. С. Шенкова, Доклады ВАСХНИЛ, 15 (1939).

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*ECOLOGY*

# RESPONSE OF IMAGO OF *EURYGASTER INTEGRICEPS* PUT. TO CERTAIN ANABIOTIC CONDITIONS

By D. M. FEDOTOV

*(Communicated by I. I. Schmalhausen, Member of the Academy, I. VIII. 1944)*

The high degree of adaptation of the internal organs of *Eurygaster integriceps* to the long periods of aestivation and hibernation, which in the Kashka-Daria province (Uzbekistan) proceed under conditions favourable for the bugs, results in that most of them are well by the end of hibernation. Those of the bugs which perish during aestivation or during the dry, warm period of hibernation largely fall victims to various predacious insects or spiders. During the cold, rainy period and in winter the predators cease to play any important rôle; the harmful influence of the abiotic agents of the medium shows a tendency to increase. But even then, however, the number of bugs that succumb to these factors is rather small. Both in valley and piedmount hibernation places we happened to find only occasional dead *Eurygaster* bugs during December, 1941 and February, 1942. The same is true of mountainous wintering places. In the collections of T. Khaidarow, among the 3935 bugs found early in March, 1942, in the mountains near the Samak village (Yakkabag region) we discovered 470 such bugs as seemed to have died long ago, while among the 5222 bugs collected at mountainous hibernation places near the Ugun village of the same region (late in February) no more than 116 such dead bugs were discovered. Sufficiently good shelters of the hibernation places in valleys, excellent shelters and snow cover in the mountains, preserve the hibernating bugs from the harmful effect of sharp temperature fluctuations during winter and early in spring. In the Kashka-Daria province these fluctuations are not strong enough to produce a lethal effect upon the bugs while in a state of torpidity (cf. observations by Smoliannikov, 1939, Rostov province).

The influence of external agents is not dangerous until the bugs begin to awake in spring; at this period they are likely to cause disturbances in the function of the internal organs of *Eurygaster integriceps*. The cold winter period is shorter in the valley, correspondingly shorter is also the period of torpidity; milder climatic conditions cause, besides, a readier mobility of the internal organs of the bugs hibernating in the valley. Such a state is dangerous only in the case of sharp and intense temperature variations that occur late in winter or in spring. But such fluctuations do but rarely occur in the valleys of the Kashka-Daria province, which are characterized by short-lived drops of temperature, rarely below —10° C, accompanied by snow falls. Even if the snow covering is but a thin one, *Eurygaster* bugs are well-preserved against such frosts in their hibernation shelter. In fact, observations made in the vicinity of the town Shakhrisiabz after a hot sunny day (March, 7), with a temperature of + 22.2°C at 1 p. m., which gave place to cold days with snow falls and morning frosts of —10° C,

revealed only isolated specimens either of freshly destroyed, or of slightly frost-beaten bugs. Most of them proved quite viable, for they still remained under their wintering shelters.

*Eurygaster integriceps* bugs become more exposed to the harmful effect of temperature fluctuations after they have left the hibernation shelters. Observations to that effect could be carried out in the piedmounts, more precisely, within the low mountainous zone (Ishkent, Yakkabag region, 1200 m above the sea level), by the end of March. After warm sunny days with thunder-showers a considerable drop in temperature, followed by snow fall, took place there. On March 25 at 7 a. m. air temperature was —7.7°C, at 11 a. m. it was—5.7° C, under snow + 0.3°, under a big stone + 3.3° C. On March 26, early in the morning, the temperature was —5° C, while towards 1 p. m. it has already attained + 9.8°, and + 19.3° at the surface of the soil. Within the subsequent days there was a considerable rise in temperature: on March 28, at 1 p. m., the temperature attained + 23.5° (data by K. V. Arnoldi). Only rare specimens of newly destroyed bugs could be recorded; the number of frost-beaten bugs was rather considerable, however. Out of the 90 bugs collected on March 26, apart from the 8 individuals that had succumbed before the frost set in, 9 became little mobile the next day, another 15 showed a mobility below the normal one. After two days, only a third of the bugs seemed to be fully alive, the rest had either perished, or were near to a fatal issue. Among the 42 bugs collected on March 27, 12 proved frost-beaten; among another lot of 60 bugs collected at the same day no more than 15 remained viable after eight days. In this region *Eurygaster integriceps* had already abandoned their wintering places, and found refuge during nights under tuffs of plants and stones. The sharp temperature fluctuations proved sufficient to reduce the vitality of the bugs under such poor shelters, and to produce fatal disturbances in the functions of their internal organs.

A still higher rate of mortality of *E. integriceps* at the period of spring awakening is observed at typical mountainous hibernation places, where, as pointed out above, but very few perished bugs are to be found in winter or early in spring. At an altitude of 2300 m (Ishkent village) we happened to find rather many dead or frost-beaten bugs under cussions of *Acantholimon* during the last ten days of April. Thus, out of the 96 bugs collected, 24 were found either to be dead, or nearly so. The main cause of mortality at this period undoubtedly consists in the sharp daily variations of air temperature, fluctuating between zero or below zero during the night, and up to + 24° C or even higher towards noon. The bugs which creep out from under their shelters are heated in the sun, after which during the night they are exposed to low temperature. Along with a reduced air humidity, this undermines the state of the bugs whose internal organs are already in an active state, disturbing their metabolism and internal equilibrium. The bugs which are rather weakened by their prolonged hibernation cannot recover and succumb to the adverse conditions.

Similar to the bugs which we found to be frost-beaten by sharp temperature fluctuations in the valley and piedmounts, the bugs become little mobile. They show a rapid and strong decrease in the amount of haemolymph, which is a typical symptom of approaching death. The internal organs which at the outset preserve their normal appearance, become poor in water, the rectum becomes flat. The intestine with the salivary glands, the odoriferous glands and the egg-tubules schrink together. The intestine becomes earthy in colour; the fat body, dirty-grey, flabby, nearly transparent. The bugs gradually dry up and perish. In this case the fatal end is brought about rather by the abrupt changes of the temperature medium than by the physical influence of temperature upon the tissues of the bugs, as in the case of freezing. When examining the bugs at their hibernation places, these symptoms are helpful in determining their condition and in predicting the survival, and consequently, the appearance of *E. integriceps* on the crops.

It is of interest to note that even such bugs as were collected in spring, after an exhausting hibernation, prove more resistant under laboratory conditions than

the well-nourished bugs of the new generation, collected at the crops and after a 1—1.5 month stay at the aestivation place. If kept under conditions of food and water deficiency, they soon become lean, poorly motile, lose their strength. The quantity of haemolymph becomes reduced in them, and so does the fat body. The intestine shrivels, the contents of the mid gut, filled while feeding on the crop, decreases, air bubbles are observed in it. Large amounts of dark excretum are accumulated in the pylorus and in the mean trunks of Malpighian vessels. The sex glands (ovaries) which first started developing, become very lean and transparent. The bugs perish in a state of extreme emaciation. Unlike this, the bugs collected by the end of hibernation are found to be much more resistant under analogous conditions. All their organs remain resistant during a long time, they do not become meagre so soon. During the long period of aestivation and hibernation the organs of the bugs seem gradually to develop a resistance which is still lacking in the bugs of the new generation when still on the crops or for a long period during aestivation. If we are to judge by the internal status of the bugs during aestivation and at the time of their autumn activity(1), this resistance sets in after the time the bugs pass to hibernation, upon their autumn migration.

From what has been said above two practical conclusions are to be made. First, chemical substances are likely to be more efficient if applied to bugs of the new generation, feeding on crops or during aestivation. Secondly, for laboratory purposes it is expedient to collect them after the period of autumn activity, but before winter frosts set in.

Observations have shown that females are more resistant than males, both in nature and under laboratory conditions. As a rule, among the perished bugs one finds, the number of males exceeds that of females. In one of our experiments involving 23 males and 63 females, the survival ratio was 2 and 30, respectively. In another experiment the respective figures were 6 and 28 from a total of 34 survivers, *etc.* The higher rate of mortality in males as compared to females, observed by the end of hibernation and during the awakening period, when there are sharp temperature fluctuations, may probably be put down to the circumstance that, owing to the proceeding development of their testes, males are more liable to emaciation than females, whose ovaries are in a state of diapause during hibernation. Yet, under laboratory conditions, males of the new generation, caught upon crops or at aestivation places, are also found to be less resistant than females. This is evidence of a higher vitality of females of *Eurygaster integriceps* in general. Records of bugs collected in the course of a year at any developmental stage of *E. integriceps*, have shown an excess of 13.6 per cent in favour of the females. According to my personal observations, however, the numerical relation may become still more in favour of the females, or else tend towards parity, or even change in favour of males, during the various periods of the life of *E. integriceps*, and even within the same period. The same observation has been made by A. A. Peredelsky on crops in the valley. The biology of *E. integriceps* and the biotic agents which underly the numerical sex relations of this bug are to be studied in detail, in order to be able to give a plausible explanation to the high rate at which this pest propagates.

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REFERENCES

[1] D. M. Fedotov, C. R. Acad. Sci. URSS, XLII, No. 9 (1944).

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*PLANT PHYSIOLOGY*

# EXCHANGE IN THE FLOODED SEEDLINGS OF RICE

By P. S. ERYGIN

*(Communicated by A. A. Richter, Member of the Academy, 13. IX. 1944)*

Both in old and new regions of rice cultivation the rice fields are flooded. This procedure brings about high mortality among the young plants. The reaction of the young plants to flooding, in particular in the case of complete submersion of the seedlings, has not been studied([3]). Some time ago this made us undertake a study of the cause of death of the submerged seedlings([1]). It has been found that disturbance of respiration was one of the principal causes of death of the seedlings which were completely submerged. In order to study this problem in more detail, a number of experiments were arranged during the summer seasons of 1938—1941.

The results of these experiments are reported below.

The seedlings of rice were produced in cemented trenches on plots which measured 0.5 $m^2$ each. Seeds which just began to sprout were planted to a depth of 1 cm.

The plants were 2 cm apart, the middles being 10 cm wide. Three types of water regime were established: 1) flooding to a depth of 20 cm; 2) same to a depth of 1 cm; 3) moistening (no layer of water whatever). The reaction of the seedlings of rice to flooding was studied by determining the weight of the seedlings, and carbohydrate and nitrogenous substances (after Smirnov([2])).

The results of determinations of the weight of the plants are presented in Table 1.

Table 1

Weight of Seedlings Subjected to Flooding
(10 individuals) in g

| Growing conditions | Age of seedlings in term of leaf formation | | | | |
|---|---|---|---|---|---|
| | 1st leaf | 2nd leaf | 3rd leaf | 4th leaf | 5th leaf |
| Moistening | 0.048 | 1.135 | 0.358 | 0.868 | 1.50 |
| Flooding: | | | | | |
| Layer of water 1 cm thick | — | 0.127 | 0.424 | — | 2.50 |
| Same, 20 cm thick | 0,031 | 0.071 | 0.173 | 0.767 | 2.75 |

The seedlings which had developed under the condition of complete submersion (20 cm of water) had half the weight of those grown on moistened plots. Besides, the rate of the accumulation of dry matter decreased with the age of the plants.

If the weight of the seedlings from unflooded plots be put at 100 at the moments of full growth of the 1st, 2nd, 3rd, 4th and 5th leaves, the weight of the flooded seedlings would be 64.6; 52.5; 48.1; 88.4 and 183.0, respectively. Relative decrease in weight was observed till the formation of the 4th leaf (48.1), *i. e.* during the period when the seedlings were completely submerged. With the appearance of the fourth leaf above the water level, the rate of the accumulation of dry matter increases, and towards the time of tillering (5th leaf) the weight of the flooded seedlings not only attained that of the seedlings grown on moistened plots, but even surpassed it. The inhibitory effect of the water layer took place only in the case of complete submersion, since, when the layer of water was only 1 cm deep, the weight of the seedlings approached that of the seedlings grown on moistened plots.

Determinations of the weigt of endosperm at the age of the formation of the 3rd leaf have similarly demonstrated the existence of an inhibitory effect of the water layer: the weight of 100 grains with submersion was equal to 0.82 g, while in the case of moistening it was 0.64 g; consequently, the reserve stuff was consumed slower with submersion than without it.

The main part of the dry matter consists of carbohydrates, both in the caryopsis and in the young plant. It was of interest, therefore, to follow up their proportion in the above-ground parts of the seedling. The results of determinations of the carbohydrates are represented in Table 2 (averages for the five ages).

Table 2

Carbohydrates in Leaves of Seedlings of Rice Subjected to Flooding
(mgs per 1 g of dry matter)

| Form of carbohydrates | Flooding, layer of water | | Moistening |
|---|---|---|---|
| | 20 cm deep | 1 cm deep | |
| Monosaccharides | 15.6 | 20.9 | 20.6 |
| Saccharose | 57.0 | 82.4 | 81.6 |
| Maltose | 0 | 0 | 0 |
| Starch | 37.7 | 69.7 | 59.2 |
| Hemicellulose | 110.6 | 80.2 | 64.0 |

Under the conditions of flooding there was a noticeable decrease in the proportion of soluble carbohydrates contained in the leaves. No sharp reduction was caused, however. The presence of starch indicates that no cessation of carbohydrate synthesis took place in the flooded seedlings. This conclusion was supported by the behaviour of the hemicelluloses which showed even an increase under flooding.

The direction of the transformation of carbohydrates changed under the influence of flooding: thus, hemicellulose was stored along with the starch.

The results of the parallel determinations of nitrogen are presented in Table 3.

At the age of two leaves the proportion of the protein nitrogen remained nearly unchanged, both in the seedlings grown on moistened soil and with flooding with 1 cm deep layer of water. Flooding with a 20 cm deep layer of water caused a noticeable reduction of proteins as compared to the case of flooding to a depth of 1 cm.

The leaves which were submerged into the water usually died soon as a result of a rapid senescence. Senescence of the leaves took place also in seedlings from the moistened soil, but not until the appearance of the fourth leaf, *i. e.* immediately before tillering.

The above data on the dry weight, carbohydrates and the protein nitrogen prove the existence of an inhibitory action of a layer of water when the latter covers the seedlings completely. The cause of the death of the seedlings, however,

Table 3

**Total and Protein Nitrogen in Leaves of Flooded Seedlings of Rice**

| Age of seedlings | Depth of water layer | | Moistening |
|---|---|---|---|
| | 20 cm | 1 cm | |
| | Total nitrogen in mgs per 1 g of dry matter | | |
| First leaf . . | 76.5 | 85.0 | 117.1 |
| Second » . . | 38.7 | 47.1 | 58.1 |
| Third » . . | 31.3 | — | — |
| Fourth » . . | 21.2 | 28.1 | 22.2 |
| | Protein nitrogen in per cent to total | | |
| First leaf . . | 98.5 | 96.0 | 96.5 |
| Second » . . | 94.0 | 96.9 | 97.2 |
| Third » . . | 92.7 | — | — |
| Fourth » . . | 90.6 | 94.1 | 89.2 |

is neither starvation nor the disturbance of exchange caused by it: the accumulation of dry matter continues in the submerged seedlings, the reserve carbohydrates are not fully consumed, and the breakdown of proteins does not reach a great degree.

We are to believe, therefore, that the main cause of the death of the seedlings of rice when completely submerged under the water is the disturbance of respiratory gaseous exchange, as observed by us earlier.

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REFERENCES

[2] А. И. Смирнов и сотр., Гос. ин-т табаковедения, вып. 46 (1928). [3] E. B. Copeland, Rice, London, 1924. [3] П. С. Ерыгин, Тр. рисовой оп. станции, вып. 7. 53 (1937).

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*PLANT PHYSIOLOGY*

# A FIELD METHOD FOR ESTIMATING RUBBER CONTENT IN LIVE ROOTS OF RUBBER PLANTS

By M. S. NAVASHIN and A. F. CHEREDNICHENKO

*(Communicated by A. A. Richter, Member of the Academy, 22. III. 1945)*

Selection for chemical properties is impossible without a method which would afford a large scale inspection of plants. There is no such method available in the rubber plant breeding which would answer in its efficiency the least requirements of the breeder. This is especially true of kok-saghyz which is subject to an exceedingly high individual variation.

In our search for such a method while working on the production of tetraploid kok-saghyz, we came to the idea that the most reasonable way of estimating rubber content would be the analysis of the latex flowing out the wounded root.

The rubber content of the root depends on both the concentration and the amount of the latex. The wide variation in the percentage of rubber in individual roots should therefore in the first place be a combined result of the variation in the concentration and amount of latex.

The dry weight of the latex in kok-saghyz consists, on the average, to three quarters in the pure hydrocarbon of the rubber. The dry weight of the latex thus permits, in the first approximation, to judge of its quality. The dry weight of the latex of kok-saghyz varies greatly, its average being about 45 per cent(1). Our determinations yeilded analogous figures for the tetraploid kok-saghyz (Table 1).

Table 1

Dry Weight of Latex of Tetraploid Kok-saghyz

| Dry weight, % | 10 — 19 | 20 — 29 | 30 — 39 | 40 — 49 | 50 — 59 | 60 — 69 | 70 — 79 |
|---|---|---|---|---|---|---|---|
| Number of roots . . . . | 4 | 14 | 42 | 50 | 51 | 9 | 2 |

Average 44.6 per cent

The first part of the problem consisted in finding an easy and rapid, but at the same time, dependable method for estimating the rubber content in the latex. Among several possible ways of doing so we have selected the nephelometric principle which has not been applied as yet; the concentration of the matter forming a suspension or an emulsion can notably be found by determining the opalescence.

Rubber is contained in the latex in the form of small particles (globules) suspended within the serum. As the theory is somewhat complicated, we have decided to compare empirically the results of nephelometric determinations with the data of direct gravimetrical analysis.

The very simple method for estimating opalescence worked out by us consisted in the following. A weighed portion of the latex, no less than 15 mg, taken with the aid of a torsion balance from the surface of a fresh cut of the root, is diluted with tap water in a large test-tube until it becomes possible to read through the resulting opalescent liquid printed characters (in falling light). It proved inconvenient to measure the degree of opalescence by the quotient found by dividing the number of cm³ of water spent for the dilution by the number of mg of the latex (*i. e.* the inverse of the value of dilution multiplied by 1000). This quotient will further be referred to as the «opalescence number». Preliminary tests have shown that the sensitivity of this method was quite satisfactory and permitted, with some practice, of an estimation to 1 or 2 tenth of a unity. Table 2 contains the results of parallel determinations of opalescence and of dry weight proportion in the latex of one-year-old roots of tetraploid kok-saghyz. In Fig. 1 the same data are presented in the form of a correlation diagram.

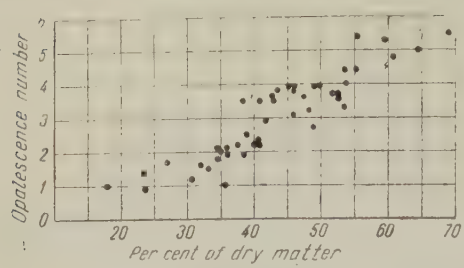

Fig. 1

Table 2

Opalescence and Weight per cent of Dry Matter in Tetraploid Kok-saghyz

| Opalescence number | Dry matter % | Opalescence number | Dry matter % | Opalescence number | Dry matter % | Opalescence number | Dry matter % | Opalescence number | Dry matter % |
|---|---|---|---|---|---|---|---|---|---|
| 0.9 | 23.9 | 2.0 | 35.0 | 3.1 | 46.0 | 4.0 | 53.8 | 5.0 | 64.3 |
| 1.0 | 35.7 | 2.1 | 36.1 | 3.2 | 48.3 | 4.4 | 55.2 | 5.3 | 59.6 |
| 1.0 | 18.0 | 2.1 | 34.5 | 3.3 | 53.8 | 4.4 | 53.5 | 5.4 | 55.4 |
| 1.2 | 30.7 | 2.2 | 37.7 | 3.5 | 38.3 | 4.8 | 60.9 | 5.5 | 69.1 |
| 1.4 | 23.5 | 2.2 | 40.8 | 3.5 | 43.1 | — | — | — | — |
| 1.5 | 33.3 | 2.2 | 40.1 | 3.5 | 41.0 | — | — | — | — |
| 1.6 | 32.1 | 2.3 | 40.8 | 3.6 | 43.0 | — | — | — | — |
| 1.7 | 27.0 | 2.5 | 39.0 | 3.6 | 52.6 | — | — | — | — |
| 1.8 | 34.7 | 2.8 | 48.9 | 3.6 | 47.5 | — | — | — | — |
| 1.9 | 36.2 | 2.9 | 41.9 | 3.7 | 52.0 | — | — | — | — |
| 1.9 | 38.7 | — | — | 3.7 | 52.3 | — | — | — | — |
| — | — | — | — | 3.8 | 46.0 | — | — | — | — |
| — | — | — | — | 3.8 | 43.6 | — | — | — | — |
| — | — | — | — | 3.9 | 46.0 | — | — | — | — |
| — | — | — | — | 3.9 | 49.7 | — | — | — | — |
| — | — | — | — | 3.9 | 49.0 | — | — | — | — |
| — | — | — | — | 3.9 | 45.1 | — | — | — | — |
| Average 1.5 | 31.0 | 2.3 | 39.5 | 3.6 | 46.9 | 4.4 | 55.8 | 5.3 | 62.1 |

From the data contained in Table 2 and Fig. 1 it follows that the concentration of the latex can be rather safely derived from estimation of opalescence.

The method employed by us could record only the suspended particles of rubber, without evaluating the other constituents; these latter substances either remained in a state of true solution, or formed a flocky sediment upon the dilution of the latex with water. This circumstance is in favour of our method which consequently affords a direct determination of the most important constituent, the rubber. Direct observations have shown that the opalescence of the water solutions of the latex is in fact dependent solely upon the rubber content. Thus, the latex of the plants practically containing no rubber (common dandelion, chicory, *Sonchus*, Morning glory, *etc.*) gave nearly limpid solutions (the «opalescence number»

being only a few tenth), since all the substances suspended in it immediately fell out when diluted with water.

It is of interest to note that the latex of plants containing no rubber invariably produced a muddy pink coloration, similar to that obtained in the test for oxidase with guajac resin. On the contrary, rubber-containing latex remained milky-white when diluted with water.

The method suggested here thus permits of an estimation of the concentration of latex with a satisfactory precision. In what follows we shall describe further simplifications of the method, which make it applicable under field conditions.

A simple and rapid method for determining rubber content in the latex is by itself of material importance. Our final object was, however, to estimate the rubber content in the root, *i. e.* to determine the rubber-producing ability of the plant.

The results of parallel determinations of the opalescense numbers and of the rubber content of the roots in per cent are presented in Table 3 and Fig. 2 (the method of extraction with benzene was employed).

As may be observed from their examination, there exists beyond doubt, on the average, a positive correlation between the concentration of the latex and the rubber content in the root. This correlation is the clearer, the higher the concentration of the latex. However, in a number of instances there are exceptions to the rule. An analysis of these exceptional cases has led to the following conclusions.

The discrepancy between the rubber content in the latex and that in the root should naturally depend on the variation in the amount and composition of the latex. The former factor remained unanalysed (for lack of a suitable method for estimating the amount of latex in the root); regarding the latter an interesting conclusion could be made. The comparison of the rubber samples precipitated with alcohol from the benzene extract has shown the quality of rubber to vary widely from root to root, from a white elastic product to a dark, sticky, and in some cases rubber unlike substance showing no elasticity. Roots showing high concentration of latex (high opalescence number) invariably yielded good white and elastic rubber; on the contrary, those which received lowest mark with regard to latex, gave products showing sca-

Table 3

Opalescence Number of Latex and Rubber Content in Roots of Tetraploid Kok-saghyz (in air dry mass)

| Opalescence number | Rubber per cent in individual roots | | | | | | | | | | | | | | | | | | | | | | | | | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | |
| 1.0—1.9 | 1.0 | 1.4 | 2.0 | 2.0 | 0.0* | 2.1 | 1.2 | 5.5 | 0.0* | 0.0* | 4.4 | 3.2 | 1.8 | 3.3 | 6.4 | — | — | — | — | — | — | — | — | — | — | — | — | 2.3 |
| 2.0—2.9 | 0.7 | 2.8 | 0.6 | 0.4 | 0.9 | 2.8 | 0.6 | 0.0* | 0.9 | 1.5 | 1.9 | 4.9 | 2.0 | 3.1 | 3.9 | 5.3 | 10.0 | 5.3 | 4.8 | — | — | — | — | — | — | — | — | — | 2.8 |
| 3.0—3.9 | 3.8 | 1.3 | 5.8 | 2.5 | 0.0* | 5.0 | 5.2 | 3.7 | 5.4 | 5 7 | 6.1 | 3.9 | 3.6 | 4.9 | 2.7 | — | — | — | — | — | — | — | — | — | — | — | — | — | 4.0 |
| 4.0—4.9 | 3.6 | 4.5 | 3.1 | 3.9 | 7.5 | 3.4 | 1.3 | 5.7 | 4.3 | 3.3 | 3.7 | 10.8 | 5.7 | 7.5 | 8.7 | 3.9 | — | — | — | — | — | — | — | — | — | — | — | — | 5.5 |
| 5.0 and above | 5.8 | 3.3 | 5.5 | 3.0 | 3.0 | 8.6 | 5.1 | 4.5 | 3.1 | 3.7 | 4.5 | 5.9 | 3.9 | 4.8 | 6.1 | 8.6 | 6.1 | 5.2 | 5.3 | 12.0 | 9.8 | 14.8 | 5.7 | 4.9 | 12.8 | 10.0 | 9.6 | 7.2 | 6.4 |

* Figures lacking significance.

reely any characteristics of rubber. It follows that the estimation of the root by the latex permits, first, to select plants wich produce the best rubber, and secondly, that the discrepancy between the data of latex and total root analysis may partly depend on the defects of the method which unites in the column «rubber» anything that is extracted with benzene and precipitated by alcohol, while the estimation of opalescence records the pure rubber only. The possibility is not excluded, therefore, that with better analytical methods the correspondence of the figures will be a far better one.

A further conclusion derived from the data presented above, as is obvious from Fig. 2, is that the discrepancy between the figures is the smaller, the higher

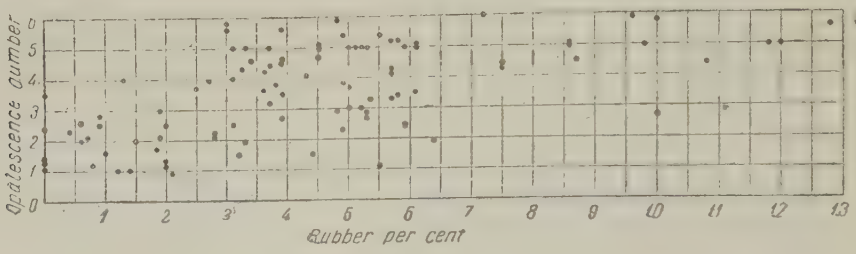


Fig. 2

the opalescence number, *i. e.* that roots showing high opalescence numbers are invariably richer in rubber. This circumstance is of great importance, since it demonstrates the possibility of selecting the most productive plants according to their latex only. The reason for this correlation may be with a good deal of probability ascribed to a correlation between the intensity of rubber formation and the development of the laticiferous system.

In concluding we wish to describe the simplified modification of our method, which is applicable under field conditions to mass selection of the most productive roots. The «equipment» is limited to a test-tube with a strip of printed text fastened to it, and a thin glass rod. Instead of weighing, a drop of latex is taken from the surface wound of a inflicted by cutting off the end of the root. The drop is allowed to fall freely into the test-tube which must preliminarily be filled with water to the mark. After stirring, the printed text is observed through the diluted latex contained in the test-tube, and, if the text is readable, the root is rejected; if, on the contrary, the opalescence latex is so great as to make reading impossible, the root is considered deserving propagation.

This method requires no trained force and reduces the expenditure of time (otherwise required for weighing, measuring and gradual addition of water, computations). Untrained hands can manage it. The method is highly efficient, since the estimating of one root, upon some practice, will take about 1 minute only. It may naturally be applied not only to mass selection, but to group selection, as well. The scheme will depend upon the standard set; with the highest standard there will be selected a small group of plants of a record-breaking rubber productivity.

One should think that with the high variation in rubber content in the roots of kok-saghyz (four fractions of a per cent to twenty per cent and even more) mass selection, which was practically impossible as yet, will lead within a short period to a considerable shift towards the increase in rubber content.

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REFERENCES

[1] А. А. Прокофьев, Сборн. Промышленные каучуконосы СССР, М., 1938.

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*EXPERIMENTAL MORPHOLOGY*

# EXPLANTATION OF NEURAL CRESTS IN *AMPHIBIA*

By J. A. VINNIKOV

*(Communicated by I. I. Schmalhausen, Member of the Academy, 9. VIII. 1944)*

The presumptive cell material of neural crests of axolotl embryos at the gastrula and neurula stages was studied by the tissue culture method.

Being located at these development stages near the borderline between the epidermal and neural rudiments, the neural crests are represented by the ectodermal region which differs but little from the other parts of the ectoderm. They are composed of a stratified layer of large extended cells filled with yolk. At the neurula stage the cell material of the neural crests is somewhat protruding above the surface of embryo, dividing the presumptive epidermis from the neural plate. In a whole embryo, the derivatives of the neural crests take part in the formation of the internal milieu of the embryos. They give rise to the so-called mesoectoderma, the cartilages of the hyioid and visceral skeleton, larynx cartilages including, the pigment elements, the medullary integumentary meninges, the peripheral glia, the spinal and sympathetic ganglia.

The neural crests of the embryos, washed after the removal of the yolk membrane by means of repeated transfer of the material through 15—20 portions of sterile saline, were divided into definite parts and then explanted by the hanging drop method in a nutrient medium consisting of rabbit plasm and embryonic extract from 10-day chick embryos. The plasm and extract were diluted by one third with saline hypotonized after Holtfreter. The explantation medium was therefore more or less similar to the internal milieu of an organism as to its physiological peculiarities. In addition, it represented a solid fibrinous clot.

Part of the material was explanted into a hanging drop of Holtfreter's solution without adding plasm. Therefore, in this series of experiments the explantation milieu was liquid. In some cases the embryonic extract was then added to make, as in the case of the solid nutrient medium, the proliferation of the embryonic element somewhat more active. However, no structures were observed whose development might be put down to the inductive influence of the embryonic extract. The period of cultivation was no less than 3—4 months. The subsequent passages were carried out every 10—20 days. A total of more than 20 series of experiments were performed in this way. The total number of explants studied *in vivo* and after fixation was over 300.

A zone of intense growth was observed around the fragment explanted after 2—3 days of cultivation. At the beginning it consisted of polymorphic indifferent elements connected with one another by cell processes and filled with yolk. At the 5—8th day of cultivation the cells of the growing zone, as well as the cells of the central bit, showed a great variety of cytological and histological differentiations. The explants taken from the tail and body parts of the neural crests showed *in vitro* a development of melanophores and lipophores ([1–4]), as well as elements

similar to neuroblasts with peculiar branched processes ([5–6]). The head parts of the neural crests, alongside of the structures just mentioned, gave rise to epithelioid membranes which in respect to the morphological peculiarities of their cell elements were similar to the medullary integumentary meninges of the vascular plexus ([7,8]). Moreover, in all the cultures started from the material of the neural crests there were occasionally observed elements growing like grass and not connected with one another.

Observations on cultures *in vivo*, as well as the study of fixed material, allowed us to establish a number of new details characteristic of the differentiation of the structures of the growing zone. The transformation of indifferent embryonic cells into melanophores or lipophores was accompanied not only by changes in their body form, but by changes in their internal structure. The first step of these changes was an increase in the size and a flattening of the cells, accompanied by the formation of numerous vacuoles in the protoplasm. There was also observed a discharge of large yolk granules from the cell body into the surrounding milieu, where they occasionally remained during a long period. The embryonic egg pigment was gradually dissolved and disappeared. Then, as a result of contraction, the body of the cell decreased in size, this process leading to breakages in those parts of the cell where vacuolization of the protoplasm was especially strong. The processes under consideration took also the form of a peculiar clasmacytosis of the differentiating elements, consisting in that entire regions of the protoplasm were isolated from the cell body by constriction in the form of droplets.

As a result of the processes described above, pigment elements arose of baroque outlines, supplied with processes. They were either free, or connected with one another by means of cytodesmoses. These protoplasmic outgrowths can either stretch to a considerable length, or be drawn back.

Simultaneously with changes in shape of the cells, a new pigment developed in the protoplasm, its development being probably independent of the pre-existent pigment dissolved. As the cells grew older, the bright-brown pigment granules in the melanophores and the lemon-yellow granules in the lipophores became considerably darker, assuming brown-black or copper-yellow colour, respectively. Pigment granules, few in number and arranged separately, were the first to appear. Along with the dissolving and disappearance of the yolk the granules increased considerably both in size and in number. The arrangement of the pigment in the protoplasm of the cell was inconstant and changed many times. Pigment granules forming beads or chains were sometimes arranged in the form of rays stretching from the nucleus to the periphery of the cell. Such a picture of yolk distribution was sometimes disturbed by the presence of small regions free of the pigment. The arrangement of the pigment here described was sometimes observed only in a definite part of the cell. The pigment elements and especially the lipophores upon mitotic division of their nuclei became, as a rule, binucleate. But after some time the protoplasm of such elements also divided, and the cells arisen became uninucleate. All the pigment elements, procumbent on the mica or fibrin, overlapping one another and interlacing, formed nets, strands and the like. They represent a very convenient material for observation *in vivo* during a long period.

Differentiating elements, similar to neural elements, very soon become free of the embryonic pigment. They are distinguished by their large nuclei with a very high refractive index. These nuclei are surrounded with a small ring in which separate large yolk granules and thin protoplasmic processes are observable. These distal ends of the processes, which are supplied with characteristic branches and growing bulbs, serve them to come into contact with other elements of the growing zone. Fibrillary structures were well seen inside the neural fibres. Part of the fibres, apparently of the neural ones, have their ends free, extending rather far into the surrounding fibrin. The fibres can form collaterals, and, intertwisting with one another, lead to the formation of a complicated network. All the elements observed had, as a rule, two processes directed towards the oppo-

site sides (bipolars). Such elements were, for the most part, developed in small cavities of liquefaction of the fibrin, in the neighbourhood of the fragment explanted.

The flattened membranes were parts of the growing zone that did not change their compound structure during a long period. The elements of such membranes soon became free of the large amount of yolk and embryonic pigment, they were filled with, and no pigment developed instead. The polygonal outlines of the cells and the regular cell membranes that can be traced between them are very similar to those of the epithelial structures of the medullary integumentary meninges. On fixed preparations transparent fibrous elements were often seen in the protoplasm of such structures.

Those elements of the zone of growth, which look like «growing grass» and are independent of or partly connected with one another, were supplied with a small amount of yolk and deprived of pigment. In respect to the lengthened body form supplied with processes, the character of their nuclei and vacuolated protoplasm, these elements were rather similar to the growing *in vitro* mesenchyme elements described in explants taken from other objects. We failed to establish more exact criteria for determining their true nature. It is quite probable that they are of mesoectodermal origin ([9,10]).

To make the experimental conditions approach, as closely as possible, those of developing embryos, a number of explants, taken from the head region of neural crests and cultivated in a hanging drop of saline, were first wrapped into epidermal sacks. Inside of these explants, there was formed a milieu of their own, that was separated from the explantation milieu by the epithelium ([11]). In some of these vesicles by the 7—8th day of cultivation there were found small cartilage regions irregular in outline and arranged at some distance from one another. Apparently, they corresponded to some elements of the visceral skeleton ([12,13]). The pigment and separate mesenchyme-like elements were occasionally found beneath the epithelial wall of the vesicle. The small number of cartilage differentiations might be accounted for by the lack in the internal explantations milieu of such influences, as occur in the development of the corresponding cartilage apparatus of an integer embryo. Neural differentiations were also observed on rare occasions.

Structures of the growing zone of the explants taken from the neural crests were able to survive during a long period without noticeable changes. Structures similar to the neural ones were the first to decrease in number and then gradually to degenerate and disappear. Then, usually by the 40—50th day of explantation, as a result of successful mitotic proliferation, disappeared differences between the epithelioid and friable mesenchyme-like cell elements. Those pigment elements which permanently changed their form and intensity of pigmentation were found to exist during the longest period.

However, owing to intense mitotic proliferation, they also became scarcely distinguishable from the other regions of the growing zone, forming together very complicated structures of the «glial type» ([14]). The conclusion to be drawn from these observations is that all the varying structures arising *in vitro* in the material in question, after losing their histological and cytological peculiarities due to proliferation, are still displaying general elementary histological potencies determined by their common origin from the same rudiment. The elements of the latter, alongside of the special histological features, are also endowed with some common «glial» determination.

Explants of the neural crests cultivated both in solid medium (plasm) and inside epithelial sacks, led to the development in all cases of such structures as display no systemic peculiarities. No independent potencies to organotypic differentiations *in vitro* could be observed.

The explantation method applied to the analysis of the nature of cell presumptive material of the neural crests confirms the resulst of the other histogenetical and experimental investigations available. At the same time, the method applied underlines the mosaicism, or «pluripotency» of this rudiment located at

the place of joining of the epidermal and neural rudiments, the extreme poles of which are the neural elements, on the one hand, and the cartilage parts obtained *in vitro*, on the other. Both can be considered as structures of the most specialized type. In connexion with their peculiar histological determination they should, accordingly, be separated not only from each other, but also from the rest of tissue components developing from the neural crests. In particular, the question is to be raised as to the histological determination of cartilages of neural origin.

Received
8. VIII. 1944.

REFERENCES

[1] L. Fischer, Arch. f. Zellf., 22 (1939). [2] J. Twitty and D. Bodenstein, J. Exp. Zool., 81 (1939). [3] G. du Schane, J. Exp. Zool., 72 (1935). [4] F. Dorris, Proc. Soc. Exp. Biol. a. Med., 34 (1936). [5] R. Harrison, Verh. d. Anat. Ges., 85 (1937). [6] Chr. Raven, Roux' Arch., 125 (1931). [7] S. Harvey and H. Burr, Arch. Neur. a. Psych., 15 (1926). [7] Н. Каннегиссер, Арх. анат., гист. и эмбр., 23 (1940). [9] Н. Кащенко, Anat. Anz., 3 (1888). [10] Н. Гаронович, Morph. Jahrb., 20 (1893). [11] Я. Винников, Усп. совр. биол., VI, вып. 1 (1943). [12] J. Platt, Morph. Jahrb., 26 (1897). [13] L. Stone, Roux' Arch., 118 (1929). [14] Н. Хлопин, Арх. анат., гист. и эмбр., 23 (1940).

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*HELMINTHOLOGY*

# ON THE RE-ARRANGEMENT OF NEMATODES OF THE ORDER *ASCARIDATA* SKRJABIN, 1915

By K. I. SKRJABIN, Member of the Academy, and V. I. KAROKHIN

The taxonomy of important systemic groups of nematodes of the order *Ascaridata* Skrjabin, 1915, underwent no serious revision or re-arrangement within the last 30 years. Since the time when Railliet et Henry (1915) had founded the *Heterocheilidae* family, the opinion became firmly established among helminthologists that *Ascaridata* (or *Ascaroidea*, which comes to the same) embrace two families: *Ascaridae* Baird, 1853, and *Heterocheilidae* Railliet et Henry, 1915.

This point of view, backed by Yorke and Maplestone's investigations (1926), is still prevalent in helminthology.

After having analysed the morphological structure of the numerous genera making up the *Ascaridata* order with respect to their distribution among the various families, and compared the taxonomic value of such characters as underly the subdivision of the *Ascaridata* families into subfamilies, we arrive at a conclusion that a fundamental re-arrangement of the taxonomy of this order is quite imperative.

Our revision will mainy concern the *Heterocheilidae* family.

We will not touch upon the *Ascaridae* family, in so far as its universally adopted subdivision into two subfamilies: *Ascarinae* Raill. et Henry, 1912, and *Ascaridiinae* Travassos, 1919, meets with no objections on our part.

Analysis of the Modern Taxonomy of the *Heterocheilidae* Family. It is a settled opinion in helminthology that the *Heterocheilidae* family differs from the *Ascaridae* by having a glandular ventricle in the hind part of the oesophagus, and also intestinal or oesophagal blind outgrowths.

A wealth of new data have, however, been accumulated in the course of the last three decades, which are at variance with this statement. Thus, Baylis described in 1920 two genera: *Amplicaecum* and *Angusticaecum* which, though possessing intestinal blind sacs, are utterly lacking any oesophagal «ventricle»; the *Anisakis* genus, in spite of the presence of a ventricle, has no intestinal or oesophagal outgrowths; while the *Goezia* genus is distinguished by the absence of a ventricle again. No ventricle was described either for the type genus of this family—*Heterocheilus* Dies., 1839, or for the closely related *Typhlophorus* Linstow, 1906.

As well-khown, in modern helminthology the *Heterocheilidae* are subdivided into four subfamilies: 1) *Heterocheilinae* Raill. et Henry, 1912; 2) *Crossophorinae* Baylis, 1920; 3) *Goeziinae* Travassos, 1919; and 4) *Anisakinae* Raill. et Henry, 1912.

The first three families are characterized by well-pronounced and specific diagnostic characters. The *Heterocheilinae* show behind the labiae a peculiar cuticular swelling supplied with a number of longitudinal folds. Instead of these, the *Crossophorinae* have a kind of necklace consisting of two rows of cuticular fringes.

In the *Goeziinae* the whole cuticle is made up of annular swellings armed with spikelets at their hind ridge. As to the *Anisakinae*, the genera which enter the composition of this subfamily are so diversified that no distinct character can be suggested for uniting them in a single subfamily. Hence the necessity to undertake a re-arrangement of the genera within the *Anisakinae* subfamily.

However, the taxonomic re-arrangement of the *Heterocheilidae* family must not be stopped at that point.

When analysing the peculiarities of each of the four subfamilies entering the *Heterocheilidae*, we soon become aware of the fact that these, too, are lacking any distinct character which would suffice to unite them into a single family.

In other words, the amalgamation of the four subfamilies referred to above into a single family, the *Heterocheilidae*, was also due to an error which needs to be eradicated.

New Families of the *Ascaridata* Order. Our suggestiosu for the re-arrangement of the whole *Ascaridata* order are as follows.

1. The *Heterocheilidae* family should be divided into 3 independent families: 1) *Heterocheilidae* Raill. et Henry, 1915 (*sensu stricto*); 2) *Goeziidae* nov. fam.; and 3) *Anisakidae* nov. fam.

2. The *Heterocheilidae* family in its new, narrower sense should have the following diagnosis: *Ascaridata* whose cephalic ends bear, behind the labia, additional cuticular elements of the type of longitudinal ribbed or fringe-like formations. Oesophagus simple, without ventricle; the intestine gives rise to one or two outgrowths directed forward, by the side of the oesophagus. Subdivided into two subfamilies: 1) *Heterocheilinae* Raill. et Henry, 1912 (the genera *Heterocheilus* Dies., 1839, and *Typhlophorus* Linstow, 1906) and 2) *Crossophorinae* Baylis, 1920, with the genus *Crossophorus* Hempr. et Ehrenb., 1828.

3. The family *Goeziidae* nov. fam. should have the following diagnosis: *Ascaridata*, with cuticles consisting throughout their length of a series of clearly distinct annular structures whose hind edge is armed with spicules. Oesophagus with out ventricle, supplied with long glandular outgrowth directed downwards. Type and unique genus, *Goezia* Zeder, 1800.

4. The family *Anisakidae* nov. fam. Should have the following diagnosis: *Ascaridata*, with cuticles deprived of spicules or additional rib-like or fringe-like formations. Alimentary channel may show several structural modifications: oesophagus supplied with ventricle, but lacking any oesophagal or intestinal outgrowths; 2) ventricle present, and so are either intestinal or oesophagal outgrowths, or both of them; 3) oesophagus deprived of both ventricle and 1) esophagal outgrowths, whereas intestinal outgrowths are present at a number of one or two. Subdivided into 2 subfamilies: *Anisakinae* Raill. et Henry, 1912, and *Angusticaecinae* sobi. nov.

Division of *Anisakidae* into Subfamilies. An analysis of the taxonomic significance of the separate elements of alimentary organs in *Anisakidae* makes us assume that the presence or absence of a ventricle is of higher systemic value than the presence or absence of blind outgrowths of oesophagus or intestines, since the ventricle is not a mere morphological character, but is also endowed with a definite physiological function. For this reason we find it necessary to divide the *Anisakidae* into 2 separate subfamilies: 1) *Anisakinae* Raill. et Henry, 1912, whose representatives possess a glandular ventricle, and 2) *Angusticaecinae* subf. nov., which have no ventricle.

The following diagnosis is suggested for the *Angusticaecinae*: *Anisakidae*, with an oesophagus lacking either ventricle or oesophagal outgrowths. Intestinal out-

growths present at a number of one or two. To this subfamily 2 genera are referred: *Angusticaecum* Baylis, 1920, and *Amplicaecum* Baylis, 1920.

The modern taxonomy of *Ascaridata* thus takes the following aspect in our intepretation:

1. Fam. *Ascaridae* Baird, 1853, falls into 2 subfamilies: *Ascarinae* Raill. et Henry, 1912, and *Ascaridiinae* Travassos, 1919.

2. Fam. *Heterocheilidae* Raill. et Henry, 1915, consisting of 2 subfamilies: *Heterocheilinae* Raill. et Henry, 1912, and *Crossophorinae* Baylis, 1920.

3. Fam. *Anisakidae* nov. fam., falling into *Anisakinae* Raill. et Henry, 1912, and *Angusticaecinae* nov. subf.

4. Fam. *Goeziidae* nov. fam. with a single genus *Goezia* Zeder, 1880.

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REFERENCES

[1] A. Railliet at A. Henry, Bull. Soc. Pathol. Exot., V, No. 4, 56 (1912).
[2] W. Yorke and P. A. Maplestone, The Nematode Parasites of Vertebrates, London, 1926.